Library

REGISTERED No. M. 3121

PROCEEDINGS

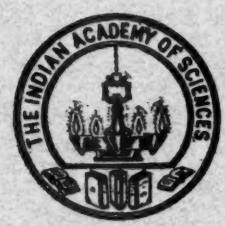
OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. V] *SECTION A* [No. 6

JUNE, 1937



Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, HESSAL, BANGALORE.

DISPERSION OF DEPOLARISATION OF LIGHT-SCATTERING IN COLLOIDS.

Part IV. Iodine, Graphite, Stearic Acid, Vanadium Pentoxide, Arsenic Trisulphide and Ferric Hydroxide Sols.

By R. S. Krishnan.

(*From the Department of Physics, Indian Institute of Science, Bangalore.*)

Received May 7, 1937.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

In several previous communications the author (1937) has pointed out that in order to determine the size, shape and structure of colloidal particles, it is important to make comparative studies of the dispersion of depolarisation of the transversely scattered light with the incident light in different states of polarisation, namely, unpolarised, vertically polarised and horizontally polarised. Measurements of the depolarisation factors ρ_u, ρ_v and ρ_h and also the extinction coefficients have been made in a large number of metallic sols, such as gold, silver, platinum, copper, selenium and tellurium. In all the cases studied a marked dependence of the degree of depolarisation on wave-length has been observed. The dispersion of depolarisation is found to be closely connected with the absorption curve. In the region of the characteristic absorption the depolarisation factors and hence the optical anisotropy show an enormous increase. This is connected with other well-known phenomena exhibited by colloidal solutions, namely, magnetic, electric and flow birefringence and their dispersion with wave-length. In the present paper the results obtained from a study of the absorption and the scattering of light in iodine, stearic acid, graphite, vanadium pentoxide, arsenic trisulphide and ferric hydroxide sols are given.

The state of polarisation of the Tyndall light in sols of arsenic trisulphide, vanadium pentoxide and ferric hydroxide was investigated by Lange (1928) by means of a spectrophotometer of the Konig-Martin type. From a measurement of the depolarisation factor with unpolarised

light alone he concluded that the particles in colloidal arsenic trisulphide were spherical in shape, whereas in iron oxide and vanadium pentoxide sols the particles were non-spherical in shape. He measured also the dispersion of the depolarisation factor ρ_u over a wave-length range from 4500 to 6500 A.U. In ferric hydroxide and vanadium pentoxide sols ρ_u was found to increase with diminution in wave-length. In arsenic trisulphide the dispersion was in the opposite direction. Very recently Mr. Subbaramaiya (1935) has measured the depolarisation factors ρ_u, ρ_v and ρ_h for an arsenic trisulphide sol using incident white light. His measurements indicate that the particles in arsenic trisulphide sol possess a small but definite optical anisotropy. His method of preparation of the sol is slightly different from that employed by Lange.

2. *Preparation of the Sols.*

Iodine sol.—Since the unprotected hydrosols of iodine were extremely unstable, changing almost instantly into a dark precipitate, a stable sol was prepared by using gelatine as the protecting agent. To 100 c.c. of a 0·4 per cent. gelatine solution were added a few drops of iodic acid solution followed by the addition of a few drops of hydroiodic acid. A sol was formed at once by the interaction of these two acids.

Stearic acid.—About 2 g. of (Kahlbaum's) stearic acid were dissolved in a few c.c. of ethyl alcohol. The resulting solution was boiled with double-distilled water for more than 24 hours so as to remove the alcohol. As the water was removed by evaporation fresh water was poured and the boiling continued till the last trace of alcohol was removed. The sol which resulted was kept in a Jena glass bottle. The sol was diluted to the desired extent before it was used for measurements.

Graphite sol or aquadag.—'Aquadag' is the technical term for the colloidal dispersion of graphite in water. The dag portion of the name is compounded from the first letters of deflocculated Acheson's graphite. Acheson's graphite is a synthetic product formed by heating amorphous carbon in the electric furnace in the presence of oxides, such as, silica, alumina and ferric oxide which are capable of yielding carbides as intermediate products. To prepare the hydrosol, the disintegrated graphite is treated with an aqueous solution of tannin containing 3–6 per cent. of the weight of graphite employed. The results are most satisfactory if a pasty mixture of graphite, tannin and water is first prepared and masticated, say for a month, before dilution with water preferably containing a small amount

of ammonia. The sol is quite stable and has an intense black colour. A small quantity of the aquadag from a sample sent by E. G. Acheson, Ltd. (London), was dissolved in 100 c.c. of double-distilled water and the solution was centrifuged in an ultra-centrifuge and the fraction containing the finest particles was separated and was used for the present investigation.

Vanadium pentoxide sol.—Colloidal vanadium pentoxide is one of the first sols in which magnetic double refraction and flow birefringence were observed. These solutions are therefore of special interest. To prepare the sol, about 1·5 g. of ammonium vanadate was triturated with 15 c.c. of 8 per cent. hydrochloric acid. The vanadium pentoxide obtained was washed out with distilled water. When the washing water began to be strongly coloured the sedimented oxide was left to stand together with about 100 c.c. of water, in which it gradually dissolved. A stable sol was obtained.

Arsenic trisulphide sol.—Numerous sulphide hydrosols may be prepared by condensation or peptization. In the condensation method we start with a suitable dilute solution of the initial material, and treat this with sulphuretted hydrogen or with a dilute solution of an alkaline sulphide ; the electrolytes which may result from the reaction are removed by dialysis. Arsenic trisulphide is chosen as a typical sulphide sol, for in this case the experimental conditions are particularly clean cut, since according to the equation

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$$

no electrolytes are formed which need be dialysed away. The sol was prepared as follows. About 0·01 g. of anhydrous arsenious acid was dissolved in 100 c.c. of pure double-distilled water and a small stream of hydrogen sulphide gas was passed through the solution till the solution was turned yellow. Then hydrogen was bubbled through the system till the smell of hydrogen sulphide was completely removed. The suspension appeared yellow with a greenish tinge in reflected light, whereas it appeared orange in transmitted light.

Ferric hydroxide sol.—In the preparation of the hydrosols of the metallic hydroxides condensation methods are most important. A freshly precipitated hydroxide may be brought into colloidal solution by washing out with water or with a solution of a peptizing electrolyte. This method is employed here for the preparation of the ferric hydroxide sol. Ferric hydroxide was precipiated from a solution of ferric chloride with ammonia solution. The washed precipitate was peptized with a dilute ferric chloride solution. The sol was reddish brown in colour.

3. *Absorption and Depolarisation Measurements.*

The methods of measuring the extinction coefficients and the depolarisation factors ρ_u, ρ_v and ρ_h from λ 2500 to 7000 A.U. have already been described in detail in the earlier parts of this series. The extinction coefficients for the six sols are given in Tables I and III. Curves of absorption are plotted with extinction coefficient as ordinate and wave-length as abscissæ. They are reproduced in Figs. 1 and 3. Values of ρ_u, ρ_v and ρ_h after applying the necessary corrections for the finite angle of convergence of the incident beam, are given in Tables II and IV. The values of ρ_u are also plotted against wave-length. The curves are reproduced in Figs. 2 and 4.

TABLE I.

Extinction Coefficients.

Wave-length λ in A.U.	Iodine	Aquadag	Stearic acid
2250	>1·8	0·13	0·6
2500	>1·8	0·135	0·53
2750	0·57	0·14	0·46
3000	0·23	0·15	0·41
3250	0·12	0·145	0·35
3500	0·09	0·135	0·3
3750	0·13	0·13	0·25
4000	0·34	0·125	0·2
4250	0·68	0·12	0·175
4500	0·97	0·12	0·155
5000	0·68	0·12	0·14
5500	0·26	0·115	0·13
6000	0·16	0·11	0·12
6500	0·1	0·105	0·11
7000	0·05	0·1	0·1

TABLE II.

Dispersion of Depolarisation ρ_u.

Wave-length λ in A.U.	Iodine			Aquadag			Stearic Acid		
	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %
2967	..	..	..	34·7	4·5	17·2	17	2·8	18·9
3650	4	..	..	32	4·5	18·9	14·8	2·5	20·8
4046	3	..	..	29·5	4·7	19·8	12·5	2·2	21·8
4358	1·5	..	..	27·1	4·7	20·8	8·8	1·7	22·8
4750	7·95	1·6	23·8	26·5	4·9	21·7	8·2	1·5	23·5
5000	6	0·5	9·5	26	5·0	22·4	7·5	1·4	24
5500	3·3	0·45	14	24·8	5·1	24·8	6·4	1·3	26
6000	2	0·2	10·5	23·8	5·3	27·1	5·3	1·2	29·8
6500	1·5	..	..	23·8	5·3	30·7	4·5	1·0	36
7000	1·2	..	..	..	..	..	..	..	..

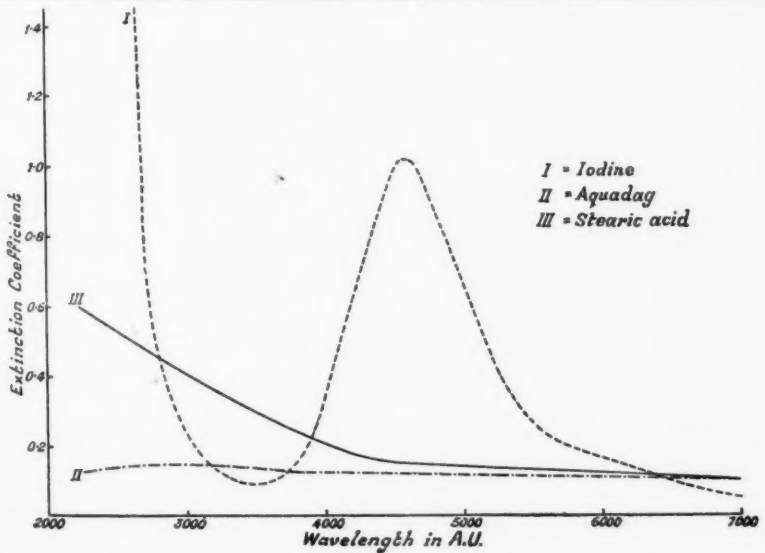


FIG. 1.
Extinction coefficients.

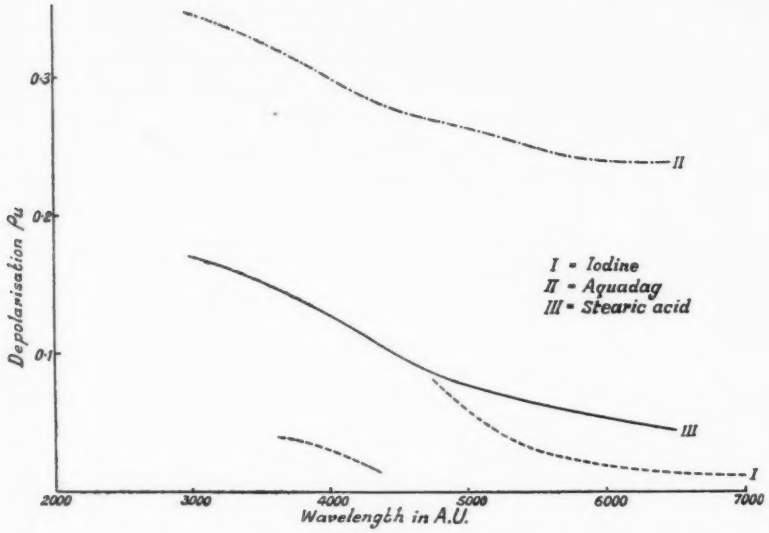


FIG. 2.

Dispersion of depolarisation factor ρ_u.

TABLE III.

Extinction Coefficient.

Wave-length λ in A.U.	Vanadium pentoxide	Arsenic trisulphide	Ferric hydroxide
3750	>3	>3	>3
4000	>3	1·8	2
4250	3	0·9	1·15
4500	1·50	0·54	0·78
5000	0·78	0·18	0·48
5500	0·34	0·11	0·34
6000	0·10	0·08	0·28
6500	0·05	0·06	0·26
7000	0·02	0·05	0·25

TABLE IV.
Dispersion of Depolarisation.

Wave-length λ in A.U.	Vanadium pentoxide			Arsenic trisulphide			Ferric hydroxide		
	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %
3650	..	..	..	17	..	..	9·5	..	..
4046	..	..	..	18·8	1·0	4·0	9·5	..	..
4358	..	..	..	24·9	1·3	4·0	9·2	..	..
4750	26	9·9	60	33·5	1·9	4·6	9·0	..	..
5000	20	9	70	39	2·2	5·3	8·6	2·5	42
5500	18	7·7	80	43·6	2·9	6·9	7·7	2·0	57
6000	8·8	3·4	90	45·5	3·1	8·2	6·5	1·9	66
6500	7·75	3	..	45·5	3·1	8·2	6·2	1·9	66

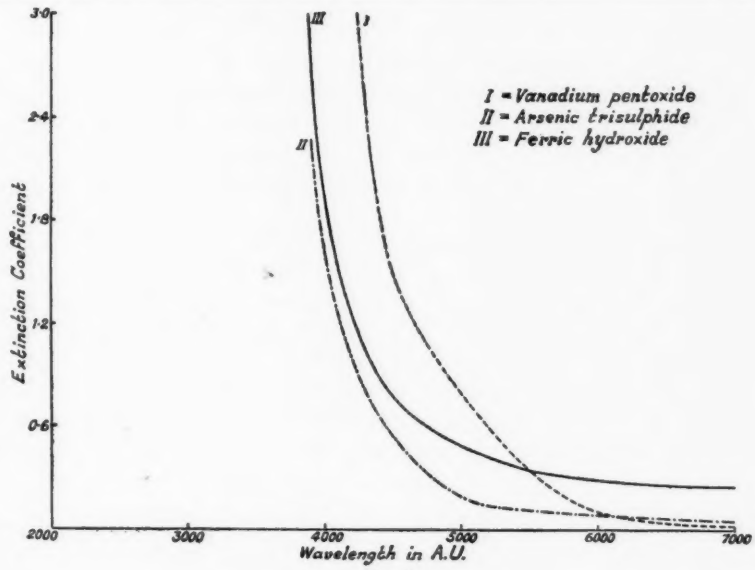


FIG. 3.
Extinction coefficients.

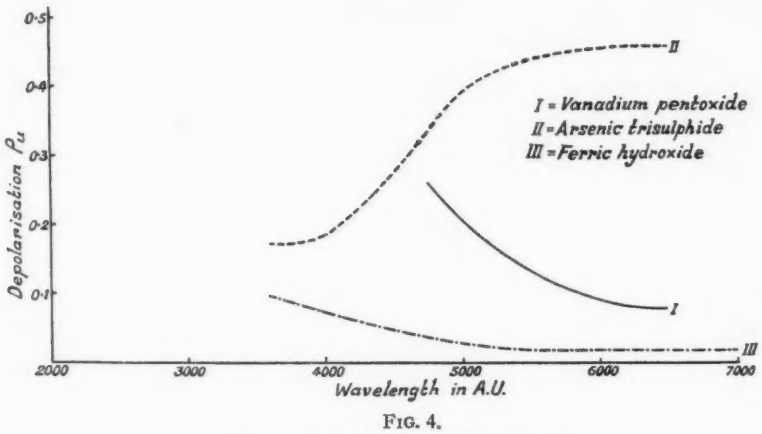


FIG. 4.
Dispersion of depolarisation factor ρ_u.

4. *Discussion of Results.*

A comparative study of the absorption coefficients, the depolarisation factors and also their dispersion with wave-length shows that the six sols investigated here can be classified under four different groups. The iodine sol which possesses a specific absorption at 4500 A.U. belongs to the first type. As in the case of gold and silver sols, so also in the case of iodine sol the depolarisation values attain their maximum value in the region of specific absorption. Stearic acid, vanadium pentoxide and ferric hydroxide sols come under the second type. These sols do not possess any region of specific absorption in the visible and the near ultra-violet regions of the spectrum. The extinction coefficient of these sols increases as one proceeds towards the ultra-violet. These sols belong to the same type as the sols of platinum, copper, selenium and tellurium. The observed dispersion of depolarisation in these cases is a size effect. The behaviour of graphite sol is slightly different from that of the sols of the second type, for in this sol ρ_v and ρ_h both diminish with decrease of wave-length. The behaviour of arsenic trisulphide is unique because as one proceeds from the red end of the spectrum towards the ultra-violet region, the absorption coefficient increases continuously, whereas the depolarisation factors including ρ_u decrease continuously.

Iodine sol.—Just as the copper sol (see Part III of this series in these *Proceedings*), iodine sol also gives comparatively small depolarisation. The observed depolarisation factor ρ_u shows a maximum at about 4500 A.U.

In this region the absorption curve also shows a maximum (see Figs. 1 and 2 and Tables I and II). The low values of ρ_v and ρ_h indicate that the particles are spherical in shape. Although a definite fall in the value of ρ_h from its limiting value of 100 per cent. suggests that the size of the particles is not small compared with the wave-length of light, the particles are only of ultra-microscopic dimensions, as is evidenced from the low value of ρ_u. These results are in agreement with the conclusions arrived at by the previous investigators from a microscopic examination of the protected iodine sol (Weiser, 1933). The microscopic examination shows that the particles are almost exclusively minute globules in rapid Brownian movement. The largest particles possess a very uniform diameter of approximately $200\mu\mu$. The particles are unmistakably spherical in shape. It is also suggested that the sol is an emulsion of liquid iodine in a saturated aqueous solution of the element. Further information that such is the case is furnished by microscopic observation of the sol formation process.

Graphite sol (aquadag).—As has already been indicated this is the only one case where ρ_u increases and ρ_v decreases with wave-length. The particles of this sol are fairly anisotropic and ultra-microscopic in size. It has been shown from other investigations that the particles are in the form of thin plates. This may probably explain the observed anomalous variation of ρ_v with wave-length.

Stearic acid sol.—In the case of the stearic acid sol a number of phenomena are known which point to a non-spherical elongated form for the particles. The finite value of ρ_v and ρ_h indicate that the micellæ are non-spherical in shape. The size of these micellæ is of the order of the wave-length of light (see Tables I and II and Figs. 1 and 2).

Vanadium pentoxide sol.—The comparatively high values of ρ_u, ρ_v and ρ_h obtained with this sol indicate that the particles are highly anisotropic. Owing to the strong absorption in the violet and the ultra-violet regions depolarisation factors could not be measured in these regions. The dispersion of depolarisation ρ_v with wave-length is rather considerable. This may be due to the fact that the particles are highly anisotropic. The way in which ρ_v varies with wave-length would seem to suggest that the particles are in the form of rods. In this sol also the size of the particles is not small compared with the wave-length of light.

Arsenic trisulphide sol.—From a comparative study of the values of ρ_u, ρ_v and ρ_h for this sol one is led to conclude that the particles are more or less spherical in shape and amicronic in size. The small but definite

value of ρ_v, however, indicates that the particles do possess a small anisotropy. This is because the difference between the refractive index of the micellæ and the intermicellar liquid in the case of this sol is great and consequently even a trace of anisotropy will be magnified in the depolarisation factors. At present it is difficult to understand why in this case alone the depolarisation factors increase *pari passu* with wave-length, whereas the absorption is stronger in the ultra-violet region than in the red region. The same phenomena has been observed by Lange (1928). X-ray studies of this sol, however, suggest that the particles are amorphous.

Ferric hydroxide sol.—As in the case of vanadium pentoxide sol, in this case also the depolarisation factors indicate that the sol contains anisotropic ultramicroscopic particles.

5. *Other Experimental Evidence.*

The double refraction occurring in many sols is closely connected with the non-spherical shape of colloidal particles. Rod-shaped double refraction is usually positive. Vanadium pentoxide (Diesselhorst and Freundlich, 1915) and stearic acid sols give positive flow birefringence. According to Diesselhorst and Freundlich arsenic trisulphide does not exhibit any detectable flow birefringence, showing thereby that the particles are of spherical shape. The double refraction produced by mechanical flow in iodine and graphite sols have not yet been investigated.

The magnetic double refraction is very pronounced in vanadium pentoxide sol (Bjornstahl, 1924). The effect is very small in the long-wave range of the spectrum but increases very quickly when approaching the short wave range. The depolarisation factors show a similar dispersion. Ferric hydroxide sol also exhibits a very high magnetic double refraction.

When vanadium pentoxide and stearic acid sols are examined under a Cardioid ultra-microscope, pronounced scintillations are observed. This is because these sols contain particles which are highly asymmetric in shape (*i.e.*, in the form of rods).

In conclusion the author wishes to record his indebtedness to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his kind interest in the work.

6. *Summary.*

Measurements of the depolarisation factors ρ_u, ρ_v and ρ_h and the extinction coefficients of iodine, graphite, stearic acid, vanadium pentoxide, arsenic trisulphide and ferric hydroxide sols are made for different wavelengths from 2500 A.U. to 7000 A.U. All these sols except the iodine sol

do not possess any region of specific absorption. As in the case of gold and silver sols so also in the case of the iodine sol the depolarisation values attain their maximum value in the region of the characteristic absorption, *i.e.*, at 4500 A.U. In stearic acid, vanadium pentoxide and ferric hydroxide sols the depolarisation factors exhibit normal dispersion. The observed dispersion in these cases is a size effect. The behaviour of the graphite sol is slightly different from that of the sols mentioned above, for in this case, ρ_v and ρ_h both diminish with decrease of wave-length. Unlike all the other sols up till now studied, the depolarisation factors in the arsenic trisulphide sol increase *pari passu* with wave-length. The depolarisation measurements indicate that the particles in the sols of iodine and arsenic trisulphide are spherical in shape, while, those in vanadium pentoxide, stearic acid, ferric hydroxide and graphite sols are non-spherical in shape.

REFERENCES.

Bjornstahl, Y., *Inaugural Dissertations, Uppsala*, 1924.

Diesselhorst and Freundlich, *Phys. Zeits.*, 1915, **16**, 413.

Krishnan, R. S., *Proc. Ind. Acad. Sci.* (A), 1937, **5**, 94, 305 and 407.

Lange, B., *Zeits. f. Phys. Chem.*, 1928, **132**, 1.

Subbaramaiya, D. S., *Proc. Ind. Acad. Sci.* (A), 1935, **1**, 705.

Weiser, H. B., *Inorganic Colloid Chemistry*, Vol. I—*The Colloidal Elements*, 1933.

A PROPERTY OF NUMBERS.

By F. C. Auluck and S. Chowla.
(Government College, Lahore.)

Received May 29, 1937.

1. Theorem. *Let* p *be a prime. If the numbers* r, r + s, r + 2s, ···, r + (m − 1) s *are congruent** (mod p) *to the numbers* 0, 1, 2, ···, (m − 1) *[not necessarily in this order], then if* m < p − 1, *we must have either* r = 0, s = 1 *or* r = m − 1, s = − 1.

Remarks. (i) If $m = p$ the numbers $r + ts$ $(0 \leqslant t \leqslant m-1)$ are congruent to the numbers 0, 1, 2, ···, $m - 1$ *for any values of* r and s provided s is prime to p.

(ii) If $m = p - 1$ the theorem is false for we can take any $s \not\equiv \pm 1$ and then choose $r \equiv s - 1$.

Proof. If the set

(1) $r, r+s, \cdots, r+(m-1)s \equiv 0, 1, 2, \cdots, (m-1)$ in some order, then by addition from (1),

$$(2) \quad mr + \frac{sm(m-1)}{2} \equiv \frac{m(m-1)}{2}$$

since $m < p$, this gives

$$(3) \quad r \equiv -\frac{(s-1)(m-1)}{2}.$$

Again, from (1),

$$\sum_{t=0}^{m-1} (r+ts)^2 \equiv \sum_{t=0}^{m-1} t^2$$

Using (3), this becomes

$$\frac{m(m-1)^2(s-1)^2}{4} - \frac{s(s-1)m(m-1)^2}{2} + (s^2-1)\frac{m(m-1)(2m-1)}{6} \equiv 0$$

or

$$\frac{m(m-1)(s-1)}{12}\left\{3(m-1)(s-1) - 6s(m-1) + 2(s+1)(2m-1)\right\} \equiv 0$$

or

$$\frac{m(m-1)(s-1)}{12}\left\{(m+1)(s+1)\right\} \equiv 0$$

since $m < p - 1$ this implies $s \equiv \pm 1$. Our result follows immediately.

2. We have also obtained a " pictorial " proof of the above theorem, by arranging the numbers on the unit circle, the number r being represented by $e^{2\pi i r/p}$.

* All congruences are to the modulus p.

ON SOME INFINITE SERIES INVOLVING ARITHMETICAL FUNCTIONS.

By S. Chowla.

(From the Government College, Lahore.)

Received May 21, 1937.

1. Let

$$\{x\} = -\frac{1}{\pi} \sum_{n=1}^{\infty} \frac{\sin(2n\pi x)}{n}.$$

We shall prove the

Theorem. *If* $c_n = O(n^{\phi})$ *where* $\phi < \frac{1}{3}$, then

$$\sum_{1}^{\infty} \frac{c_n}{n} \{n\theta\} = -\frac{1}{\pi} \sum_{1}^{\infty} \frac{G_n \sin(2n\pi\theta)}{n}$$

where $G_n = \sum_{d/n} c_d$, *is true for almost all* θ.

We follow the method used by Davenport to prove the special cases $c_n = \mu(n)$, $\lambda(n)$, $\Lambda(n)$ which are the well-known arithmetical functions [*Quar. J. of Maths.* (Oxford), March 1937]. Our theorem also includes the cases c_n = no. of divisors of n, etc., discussed by Walfisz and the author (*Acta Arithmetica*, Band I).

The letter D is used as a reference to Davenport's paper cited above.

2. Let

$$R_N(\theta) = \sum_{n=1}^{N} \left[\frac{c_n}{n} \{n\theta\} + \frac{1}{\pi} \frac{G_n \sin(2n\pi\theta)}{n}\right].$$

Then (D.)

$$\int_0^1 R_N^2(\theta)\, d\theta = \sum_1^N \sum_1^N \frac{c_m c_n (m, n)^2}{12 m^2 n^2} - \frac{1}{2\pi^2} \sum_1^N \frac{G_n^2}{n^2}$$

3. We shall show that the expression on the right-hand side above is 0 when $N = \infty$.

We have the formal identity

$$\sum_{1}^{\infty} \frac{G_n^2}{n^s} = \zeta(s) \times \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{c_m c_n (m, n)^s}{m^s n^s}$$

where $\zeta(s)$ is Riemann's zeta-function. For comparing coefficients of n^{-s} on both sides, we have

$$G_n^2 = \sum_{d/n} h(d)$$

where

$$h_v = \sum_{\frac{mn}{(m,n)} = v} c_m c_n$$

which is obvious since

$$G_n = \sum_{d|n} c_d$$

Putting $s = 2$ we have the desired result.

4. It now follows that the double series of Section 2 is equal to the double series

$$\begin{aligned}
&- \sum_{\text{Max}\,(m,n) > N} \frac{c_m c_n (m,n)^2}{m^2 n^2} \\
&= O\left(\sum_{m > N} \frac{c_m c_n (m,n)^2}{m^2 n^2} \right) \\
&= O\left(\sum_{m > N} \frac{m^\phi}{m^2} \sum_{d|m} d^\phi \sum_{n'=1}^{\infty} \frac{1}{(n')^{2-\phi}} \right) \\
&= O\left(\sum_{m > N} \frac{m^{2\phi+\epsilon}}{m^2} \right) \\
&= O\left(\frac{N^{2\phi+\epsilon}}{N} \right)
\end{aligned}$$

since $\phi < \frac{1}{3}$.

Since

$$G_n = O\,(n^{\phi+\epsilon})$$

it follows that the right-hand side of the second expression in Section 2 is

$$O\,(N^{2\phi - 1 + \epsilon})$$

5. We shall now show that $R_N(\theta) \to 0$ as $N \to \infty$ for almost all θ. It will be sufficent to prove that

$R_{m^3}(\theta) \to 0$ as $m \to \infty$ for almost all θ, since if $m^3 \leqslant n < (m+1)^3$ we have

$$\begin{aligned}
&| R_n(\theta) - R_{m^3}(\theta) | \\
&= O\left(\sum_{t=m^3}^{t=(m+1)^3} \frac{t^{\phi+\epsilon}}{t} \right) \\
&= O\,[m^{3(\phi-1)} m^2] \\
&= O\,(m^{3\phi-1})
\end{aligned}$$

which tends to 0 as $m \to \infty$ since $\phi < \frac{1}{3}$.

Let E_m denote the set of points θ at which

$$| R_{m^3}(\theta) | > \frac{1}{\log m}$$

then

$$\text{measure } E_m < \frac{c\,(\log^2 m)\; m^{(2\phi+\epsilon)3}}{m^3}$$

from the result of Section 4.

Let

$$E = \lim_{n\to\infty} \sum_{m>n} E_m$$

then (D.)

measure $E = 0$

since $-6\phi + 3 > 1$ for $\phi < \frac{1}{3}$.

But any point θ at which $R_{m^3}(\theta)$ does not tend to zero belongs to an infinity of the sets E_m and therefore belongs to E. Hence our result that $R_n(\theta) \to 0$ as $n \to \infty$ for almost all θ.

6. The second half of the expression for $R_N(\theta)$ is

$$\sum_{n=1}^{N} \frac{G_n}{n} \sin(2n\pi\theta)$$

since $G_n = O(n^{\frac{1}{3}+\epsilon})$ it follows from a well-known theorem of Kolmogoroff that the above sum tends to a definite limit as $N \to \infty$ for almost all θ. From the result of Section 5 it now follows that the first half of the expression for $R_N(\theta)$ also tends to a definite limit as $N \to \infty$ for almost all θ. Hence $\sum_1^\infty \frac{c_n}{n}\{n\theta\} = -\frac{1}{\pi}\sum_1^\infty \frac{G_n}{n}\sin(2n\pi\theta)$ is true for almost all θ if $c_n = O(n^\phi)$ where $\phi < \frac{1}{3}$. Our theorem is proved.

ON SOME INFINITE SERIES INVOLVING ARITHMETICAL FUNCTIONS (II).

By S. Chowla.

(*From the Government College, Lahore.*)

Received May 29, 1937.

1. We have

$$\sum_1^\infty \frac{\cos n\theta}{n} = -\log\left(2\left|\sin\frac{\theta}{2}\right|\right) \tag{1}$$

if θ is not an integral multiple of 2π. This leads us to the *formal* identity

$$\sum_1^\infty \frac{c_n \log(2|\sin n\pi\theta|)}{n} = -\sum_1^\infty \frac{G_n \cos(2n\pi\theta)}{n} \tag{2}$$

where $G_n = \sum_{d/n} c_d$ and d/n means that d is a divisor of n. We shall investigate the truth of (2) for irrational values of θ. Following Davenport (*Q.J.M.*, Oxford, March 1937) we prove.

Theorem I. *If* $c_n = O(n^\phi)$ *where* $\phi < \frac{1}{3}$, *then* (2) *is true for almost all* θ. *In particular the series on the left-hand side of* (2) *is convergent for almost all* θ.

2. We need the following definite integrals (we evaluate them *formally* but it is easy to give rigorous proofs).

From (1) if r and s are positive integers

$$\begin{aligned}
&\int_0^1 \log(2|\sin r\pi\theta|)\log(2|\sin s\pi\theta|)\,d\theta \\
&= \int_0^1 \left\{\sum_{m=1}^\infty \sum_{n=1}^\infty \frac{\cos 2mr\pi\theta \cos 2ns\pi\theta}{mn}\right\} d\theta \\
&= \tfrac{1}{2} \sum_{\substack{m=1 \\ (mr=ns)}}^\infty \sum_{n=1}^\infty \frac{1}{mn} \\
&= \frac{\pi^2}{12}\frac{(r,s)^2}{rs} \qquad (3)
\end{aligned}$$

where (r, s) is the g.c.d. of r and s. Again, from (1) it is easy to see that

$$(4)\qquad \int_0^1 \cos(2n\pi\theta)\log(2\,|\sin d\pi\theta\,|)\,d\theta$$

$$= -\tfrac{1}{2}\frac{d}{n} \text{ if } d/n$$

$$= 0 \text{ if } d \nmid n$$

3. Consider

$$(5)\qquad R_N(\theta) = \sum_{n=1}^{N}\left\{\frac{c_n \log(2\,|\sin n\pi\theta\,|)}{n} + \frac{G_n}{n}\cos(2n\pi\theta)\right\}$$

From (3) and (4),

$$(6)\qquad \int_0^1 R_N^2(\theta)d\theta = \frac{\pi^2}{12}\sum_{r=1}^{N}\sum_{s=1}^{N}\frac{c_r c_s (r,s)^2}{r^2 s^2} - \tfrac{1}{2}\sum_1^N \frac{G_n^2}{n^2}$$

In what follows we shall use

$$G_n = O(n^{\phi+\epsilon})$$

for any $\epsilon > 0$. This follows from $c_n = O(n^\phi)$ and $\sum_{d/n} 1 = O(n^\epsilon)$.

4.
$$G_n = \sum_{d/n} c_d$$

This gives

$$(7)\qquad G_n^2 = \sum_{d/n} h(d)$$

where

$$(8)\qquad h(v) = \Sigma c_m c_z$$

where m, n take all values such that $\frac{mn}{(m,n)} = v$.

Hence we have

$$(9)\qquad \left(\sum_1^\infty n^{-s}\right)\times\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\frac{c_m c_n (m,n)^s}{m^s n^s} = \sum_1^\infty \frac{G_n^2}{n^s}$$

Putting $s = 2$,

$$(10)\qquad \frac{\pi^2}{6}\sum_1^\infty\sum_1^\infty \frac{c_m c_n (m,n)^2}{m^2 n^2} = \sum_1^\infty \frac{G_n^2}{n^2}$$

5. From (10) the right-hand side of (6) is of the *order*

$$\sum_{N+1}^{\infty} n^{2\phi-2+\epsilon} + \sum_{m>N}\Sigma\frac{|c_m|\,|c_n|\,(m,n)^2}{m^2 n^2}$$

Put $n = n'd$ where $d = (m,n)$ and the second expression is of the order

$$\sum_{m>N} m^{\phi-2}\sum_{d/m} d^\phi \sum_{n'=1}^{\infty}(n')^{\phi-2} = O\Big(\sum_{m>N} m^{2\phi-2+\epsilon}\Big) = O(N^{2\phi-1+\epsilon})$$

Hence the r.h.s. of (6) is $0(N^{2\phi-1+\epsilon})$.

6. Let E_m denote the set of points θ at which

$$| R_{m^3}(\theta) | > \frac{1}{\log m}.$$

From the result of the last section,
measure $E_m < c\, m^{3(2\phi-1+\epsilon)} \log^2(m) < c.\, m^{6\phi-3+4\epsilon}$
where c denotes an absolute positive constant. Write

$$E = \lim_{n\to\infty} \sum_{m>n} E_m \tag{11}$$

Then

$$\text{Measure } E = 0 \text{ since } \phi < \tfrac{1}{3}. \tag{12}$$

If $m^3 \leqslant n < (m+1)^3$, then

$$| R_n(\theta) - R_{m^3}(\theta) | = 0\left(\sum_{t=m^3}^{t=(m+1)^3} t^{\phi-1+\epsilon}\right) \tag{13}$$

is true for almost all θ since $\log | \sin n\pi\theta | = O(\log n)$ for almost all θ.
From (13), for almost all θ,

$$| R_n(\theta) - R_{m^3}(\theta) | \to 0 \text{ as } m \to \infty \text{ if } m^3 \leqslant n < (m+1)^3. \tag{14}$$

Thus, as in Davenport,

$$R_n(\theta) \to 0 \quad \text{as } n \to \infty,$$

for almost all θ. Since $G_n = O(n^{\frac{1}{3}})$ it follows from a theorem of Kolmogoroff that

$$\sum_1^\infty \frac{G_n}{n} \cos(2n\pi\theta)$$

is convergent for almost all θ. Hence the first half of the expression (5) for $R_N(\theta)$ tends to a definite limit as $N \to \infty$ for almost all θ. This proves our theorem.

A GENERALIZATION OF THE SIMSON LINE.

By Faqir Chand Auluck.

Received May 31, 1937.
(Communicated by Dr. S. Chowla.)

Theorem. *If the feet of the perpendiculars from a point on five lines lie on a conic through the point, that point must lie on the Miquel circle of the 5 lines.*[1]

Proof. Let the 5 lines be

$$L_i \equiv p_i - x \cos \alpha_i - y \sin \alpha_i = 0 \quad (1 \leqslant i \leqslant 5)$$

The point (x_0, y_0) and the feet of the perpendiculars on the 5 lines lie on a conic if (x_0, y_0) lies on the curve

$$\begin{vmatrix} L_1 \cos^2 \alpha_1 & L_1 \cos \alpha_1 \sin \alpha_1 & L_1 \sin^2 \alpha_1 & \cos \alpha_1 & \sin \alpha_1 \\ & \cdots & \cdots & & \\ L_5 \cos^2 \alpha_5 & L_5 \cos \alpha_5 \sin \alpha_5 & L_5 \sin^2 \alpha_5 & \cos \alpha_5 & \sin \alpha_5 \end{vmatrix} = 0$$

It is easily seen that the coefficients of x^3, y^3, x^2y, xy^2 are all zero. Hence the curve is a conic.

Now let (0, 0) be the Miquel point of 4 of the lines (L_1, L_2, L_3, L_4). Then $p_i = l \sec \alpha_i$, where $2l$ is the semi-latus-rectum of the parabola touching these 4 lines. Substitution in the above determinant shows that this Miquel point [(0, 0)] lies on the above conic. Since the conic passes through all the 5 Miquel points it is the Miquel circle of the 5 lines.

[1] The locus of the point also consists of the five lines themselves. This omission was pointed out to me by Dr. S. Chowla.

ON THE SUFFICIENCY OF THE CONSISTENCY-EQUATIONS.

By B. R. Seth.

(From the Department of Mathematics, Hindu College, Delhi.)

Received February 20, 1937.

When there are no body forces we know that for any stress-system to be possible in an isotropic solid body the stress-components must satisfy besides the three body-stress equations

$$\frac{\partial \widehat{xx}}{\partial x} + \frac{\partial \widehat{xy}}{\partial y} + \frac{\partial \widehat{xz}}{\partial z} = 0, \tag{1. 1}$$

$$\frac{\partial \widehat{xy}}{\partial x} + \frac{\partial \widehat{yy}}{\partial y} + \frac{\partial \widehat{yz}}{\partial z} = 0, \tag{1. 2}$$

$$\frac{\partial \widehat{xz}}{\partial x} + \frac{\partial \widehat{yz}}{\partial y} + \frac{\partial \widehat{zz}}{\partial z} = 0, \tag{1. 3}$$

the six consistency-equations given by

$$(1 + \eta)\, \nabla^2 \widehat{xx} + \frac{\partial^2 \theta}{\partial x^2} = 0, \tag{2. 1}$$

$$(1 + \eta)\, \nabla^2 \widehat{yy} + \frac{\partial^2 \theta}{\partial y^2} = 0, \tag{2. 2}$$

$$(1 + \eta)\, \nabla^2 \widehat{zz} + \frac{\partial^2 \theta}{\partial z^2} = 0, \tag{2. 3}$$

$$(1 + \eta)\, \nabla^2 \widehat{yz} + \frac{\partial^2 \theta}{\partial y\, \partial z} = 0, \tag{2. 4}$$

$$(1 + \eta)\, \nabla^2 \widehat{zx} + \frac{\partial^2 \theta}{\partial z\, \partial x} = 0, \tag{2, 5}$$

$$(1 + \eta)\, \nabla^2 \widehat{xy} + \frac{\partial^2 \theta}{\partial x\, \partial y} = 0, \tag{2. 6}$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, η is the Poisson's ratio, and $\theta = \widehat{xx} + \widehat{yy} + \widehat{zz}$.

In many treatises* on Applied Mechanics a mistake has been made in obtaining a stress-system from the body-stress equations without reference to the consistency-equations. The stress-components thus determined do not correspond to any possible displacement in an isotropic body. In view

* See Love, *Mathematical Theory of Elasticity*, p. 22 (4th Ed.), where references to such books by Grashof and others will be found.

of this mistake the proving of the sufficiency of the consistency-equations whose necessity is well known becomes a matter of some interest.

We shall shew that, if a stress-system satisfies the nine equations given by (1) and (2), the corresponding components of displacement can be uniquely determined but for a rigid body displacement which, as we know, does not affect the state of strain in the body.

Differentiating (1. 1) with respect to x, (1. 2) with respect to y, (1. 3) with respect to z, and subtracting the last from the sum of the first two results, we have

$$2\frac{\partial^2 \widehat{xy}}{\partial x\,\partial y} = \frac{\partial^2 \widehat{zz}}{\partial z^2} - \left[\frac{\partial^2 \widehat{xx}}{\partial x^2} + \frac{\partial^2 \widehat{yy}}{\partial y^2}\right] \tag{3. 1}$$

If E is the Young's modulus and μ the rigidity, we can re-write (3. 1) as

$$\frac{1}{\mu}\frac{\partial^2 \widehat{xy}}{\partial x\,\partial y} = \frac{1+\eta}{\mathrm{E}}\frac{\partial^2\theta}{\partial z^2} - \frac{1+\eta}{\mathrm{E}}\left[\frac{\partial^2 \widehat{xx}}{\partial x^2} + \frac{\partial^2 \widehat{yy}}{\partial y^2} + \frac{\partial^2}{\partial z^2}(\widehat{xx} + \widehat{yy})\right],$$

which, if we notice that

$$\nabla^2\theta = 0,$$

becomes on using (2. 1), (2. 2), and (2. 3)

$$\begin{aligned}\frac{1}{\mu}\frac{\partial^2 \widehat{xy}}{\partial x\,\partial y} &= \frac{1+\eta}{\mathrm{E}}\left[\frac{\partial^2 \widehat{xx}}{\partial y^2} + \frac{\partial^2 \widehat{yy}}{\partial x^2}\right] - \frac{\eta}{\mathrm{E}}\left[\frac{\partial^2\theta}{\partial x^2} + \frac{\partial^2\theta}{\partial y^2}\right] \\ &= \frac{1}{\mathrm{E}}\frac{\partial^2}{\partial y^2}\left[\widehat{xx} - \eta\,(\widehat{yy} + \widehat{zz})\right] + \frac{1}{\mathrm{E}}\frac{\partial^2}{\partial x^2}\left[\widehat{yy} - \eta\,(\widehat{zz} + \widehat{xx})\right] \qquad (3.\ 2)\end{aligned}$$

Hence,

$$\begin{aligned}\frac{1}{\mu}\widehat{xy} = \frac{1}{\mathrm{E}}\frac{\partial}{\partial y}\int\left[\widehat{xx} - \eta\,(\widehat{yy} + \widehat{zz})\right]dx + \frac{1}{\mathrm{E}}\frac{\partial}{\partial x}\int\left[\widehat{yy} - \eta\,(\widehat{zz} + \widehat{xx})\right]dy \\ + \frac{\partial f_1(y, z)}{\partial y} + \frac{\partial f_2(z, x)}{\partial x}, \qquad (3.\ 3)\end{aligned}$$

where f_1 and f_2 are respectively functions of y, z and z, x only.

Similarly we have

$$\begin{aligned}\frac{1}{\mu}\widehat{yz} = \frac{1}{\mathrm{E}}\frac{\partial}{\partial z}\int\left[\widehat{yy} - \eta\,(\widehat{zz} + \widehat{xx})\right]dy + \frac{1}{\mathrm{E}}\frac{\partial}{\partial y}\int\left[\widehat{zz} - \eta\,(\widehat{xx} + \widehat{yy})\right]dz \\ + \frac{\partial f_2'(z, x)}{\partial z} + \frac{\partial f_3(x, y)}{\partial y}, \qquad (3.\ 4)\end{aligned}$$

$$\begin{aligned}\frac{1}{\mu}\widehat{zx} = \frac{1}{\mathrm{E}}\frac{\partial}{\partial x}\int\left[\widehat{zz} - \eta\,(\widehat{xx} + \widehat{yy})\right]dz + \frac{1}{\mathrm{E}}\frac{\partial}{\partial z}\int\left[\widehat{xx} - \eta\,(\widehat{yy} + \widehat{zz})\right]dx \\ + \frac{\partial f_3'(x, y)}{\partial x} + \frac{\partial f_1'(y, z)}{\partial z}, \qquad (3,\ 5)\end{aligned}$$

where f_1', f_2', f_3' are functions which may be different from f_1, f_2, f_3.

Substituting the values of $\widehat{xy}$, $\widehat{yz}$, $\widehat{zx}$ from (3. 3), (3. 4), (3. 5) in (1) and (2. 4), (2. 5), (2. 6), we get

$$\frac{\partial^2 f_1}{\partial y^2} + \frac{\partial^2 f_1'}{\partial z^2} = 0, \quad \frac{\partial^2 f_2}{\partial x^2} + \frac{\partial^2 f_2'}{\partial z^2} = 0, \quad \frac{\partial^2 f_3}{\partial y^2} + \frac{\partial^2 f_3'}{\partial x^2} = 0, \tag{4. 1}$$

$$\frac{\partial}{\partial y}\nabla^2 f_1 + \frac{\partial}{\partial x}\nabla^2 f_2 = 0, \frac{\partial}{\partial z}\nabla^2 f_2' + \frac{\partial}{\partial y}\nabla^2 f_3 = 0, \frac{\partial}{\partial x}\nabla^2 f_3' + \frac{\partial}{\partial z}\nabla^2 f_1' = 0 \tag{4. 2}$$

The equations in (4) are all consistent if $f_1 = f_1'$, $f_2 = f_2'$, $f_3 = f_3'$, and all the f's are harmonic. Let us assume that the general value of f''s is given by

$$f_r' = f_r + \phi_r, \quad r = 1, 2, 3.$$

Substituting these values in (4) we see that all the f''s in (3. 3), (3. 4) and (3. 5) can be replaced by the corresponding f's provided we add the term

$$A_1 x + A_0 \text{ and } B_1 y + B_0$$

to the right-hand side of (3. 4) and (3. 5), A's and B's being all constants. Putting

$$\psi_1 = f_1 + \frac{1}{2\mu} yz\,(B_1 - A_1) + \frac{1}{2\mu} B_0 z,$$

$$\psi_2 = f_2 + \frac{1}{2\mu} zx\,(A_1 - B_1) + \frac{1}{2\mu} A_0 z,$$

$$\psi_3 = f_3 + \frac{1}{2\mu} xy\,(A_1 + B_1) + \frac{1}{2\mu}(A_0 y + B_0 x),$$

we see that $\widehat{xy}$, $\widehat{yz}$, $\widehat{zx}$ now take the form

$$\frac{1}{\mu}\widehat{xy} = \frac{1}{E}\frac{\partial}{\partial y}\int\left[\widehat{xx} - \eta\,(\widehat{yy} + \widehat{zz})\right] dx + \frac{1}{E}\frac{\partial}{\partial x}\int\left[\widehat{yy} - \eta\,(\widehat{zz} + \widehat{xx})\right] dy + \frac{\partial \psi_1}{\partial y} + \frac{\partial \psi_2}{\partial x}, \tag{5. 1}$$

$$\frac{1}{\mu}\widehat{yz} = \frac{1}{E}\frac{\partial}{\partial z}\int\left[\widehat{yy} - \eta\,(\widehat{zz} + \widehat{xx})\right] dy + \frac{1}{E}\frac{\partial}{\partial y}\int\left[\widehat{zz} - \eta\,(\widehat{xx} + \widehat{yy})\right] dz + \frac{\partial \psi_2}{\partial z} + \frac{\partial \psi_3}{\partial y}, \tag{5. 2}$$

$$\frac{1}{\mu}\widehat{xz} = \frac{1}{E}\frac{\partial}{\partial x}\int\left[\widehat{zz} - \eta\,(\widehat{xx} + \widehat{yy})\right] dz + \frac{1}{E}\frac{\partial}{\partial z}\int\left[\widehat{xx} - \eta\,(\widehat{yy} + \widehat{zz})\right] dx + \frac{\partial \psi_3}{\partial x} + \frac{\partial \psi_1}{\partial z}, \tag{5. 3}$$

where ψ's are all harmonic and are respectively functions of (y, z), (z, x) and (x, y).†

† That harmonic values for ψ's can be found we can see by operating (5) by ∇^2. The resulting equations are merely those given in (2. 4), (2. 5) and (2. 6).

Now the strain-components are connected with the stress-components by relations of the type

$$S_x = \frac{1}{E}\left[\widehat{xx} - \eta\,(\widehat{yy} + \widehat{zz})\right], \quad \sigma_{yz} = \frac{1}{\mu}\widehat{yz} \tag{6}$$

From (5) and (6) we see that quantities u, v, w, given by

$$u = \frac{1}{E}\int\left[\widehat{xx} - \eta\,(\widehat{yy} + \widehat{zz})\right] dx + \psi_1\,(y, z), \tag{7. 1}$$

$$v = \frac{1}{E}\int\left[\widehat{yy} - \eta\,(\widehat{zz} + \widehat{xx})\right] dy + \psi_2\,(z, x), \tag{7. 2}$$

$$w = \frac{1}{E}\int\left[\widehat{zz} - \eta\,(\widehat{xx} + \widehat{yy})\right] dz + \psi_3\,(x, y) \tag{7. 3}$$

can be determined which are connected with the strain-components by the well-known formulæ

$$S_x = \frac{\partial u}{\partial x}, \quad \cdots, \quad \sigma_{yz} = \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}.$$

We shall now shew that, if $\widehat{xx}$, $\widehat{yz}$, etc., are all given, the ψ's can be uniquely determined but for a rigid body displacement. If possible, let there be two solutions, one given by ψ's and the other by ψ''s. From (6) and (7) we see that

$$\frac{\partial}{\partial x}(\psi_1 - \psi_1') = 0, \quad \frac{\partial}{\partial y}(\psi_2 - \psi_2') = 0, \quad \frac{\partial}{\partial z}(\psi_3 - \psi_3') = 0, \tag{8. 1}$$

$$\frac{\partial}{\partial y}(\psi_3 - \psi_3') + \frac{\partial}{\partial z}(\psi_2 - \psi_2') = 0, \quad \frac{\partial}{\partial z}(\psi_1 - \psi_1') + \frac{\partial}{\partial x}(\psi_3 - \psi_3') = 0,$$

$$\frac{\partial}{\partial x}(\psi_2 - \psi_2') + \frac{\partial}{\partial y}(\psi_1 - \psi_1') = 0 \tag{8. 2}$$

If we differentiate the left-hand members of (8) with respect to x, y, z, we shall obtain eighteen linear equations connecting the eighteen second differential coefficients of $(\psi_1 - \psi_1')$, $(\psi_2 - \psi_2')$, $(\psi_3 - \psi_3')$, from which it follows that all these second differential coefficients vanish. Hence we must have

$$\psi_1 - \psi_1' = u_0 - w_3 y + w_2 z, \quad \psi_2 - \psi_2' = v_0 - w_1 z + w_3 x,$$

$$\psi_3 - \psi_3' = w_0 - w_2 x + w_1 y, \tag{9}$$

where u_0, v_0, w_0 and w's are all constants. From (9) we see that ψ's and ψ''s can only differ by a rigid body displacement, and hence, subject to this restriction, they can be uniquely determined.

The consistency-equations in stress-components are, therefore, both necessary and sufficient.

STUDIES IN THE SUBSTITUTED QUATERNARY AZONIUM COMPOUNDS.

Part V. The Molecular State of Phenyldimethylazonium, Phenylmethylethylazonium, Phenyldiethylazonium, Phenylmethylbenzylazonium, Phenylpropylbenzylazonium Iodides in Dilute Solution.

By Bawa Kartar Singh
and
Mela Ram Sud.

(From the Chemical Department, Science College, Patna.)

Received May 17, 1937.

As the result of their researches on the molecular state of organic ammonium salts in solution, Turner and his collaborators[1] came to the conclusion that the degree of association of a salt depends on the following factors:—

(*a*) the nature of the base; (*b*) the character of the acid; (*c*) temperature; (*d*) the concentration of the solution; (*e*) the nature of the solvent.

In the present communication, we describe the results of molecular weight determinations, using the Lumsden-Walker method, of the salts of a new class of organic nitrogen bases, namely, the substituted quaternary azonium iodides which contain both a quinquevalent and a tervalent nitrogen atom. In order to make the results comparable, we have eliminated, as far as possible, differences arising from factors (*b*), (*c*) and (*d*). We have employed five different substituted quaternary azonium iodides and two solvents, namely, water and ethyl alcohol.

It is found that a rise in temperature, in general, brings about a reduction in the degree of association of a substance. In choosing water and alcohol as solvents* which differ in their boiling points by only 22°, we have reduced the difference due to the temperature factor as far as possible.

Continuous reduction of pressure on a gas tends to reduce the molecular state to the simplest possible, and in like manner, decrease in concentration should bring about a similar state in solution. The effect of concentration, therefore, acts in such a way that an increase in its value brings about an increase in the degree of association, unless chemical combination occurs between solvent and solute, in which case there is decrease in the degree of association with increasing concentration. It is with this object that we have employed very dilute solutions in these experiments, the concentration in most cases ranging from 0·6 to 1·5 per cent. As regards the medium,

[1] Turner, *J.C.S.*, 1911, **99**, 880; 1912, **101**, 1923; Turner and Pollard, *ibid.*, 1914, **105**, 1751.

* See page 523.

the Nernst-Thomson rule[2] asserts that dissociation of the solute will be allowed or restricted according as the dielectric constant of the solvent is high or low, and conversely, association is allowed to the fullest extent by a medium of low dielectric constant. This rule was borne out by measurements on amides and anilides,[3] though three substances, namely, phenylurethane, methylacetanilide and ethylacetanilide were found to afford no test of the Nernst-Thomson rule. Among other substances, which do not follow the rule, benzoic acid may be cited. It is associated in water, but not in ethyl alcohol or ether.[4] The results obtained with salts of organic ammonium bases by Turner and his collaborators (*loc. cit.*) generally support this rule, though exceptions in their case also are not wanting; namely, diethyl ammonium chloride, which is distinctly associated in acetonitrile, of high dielectric constant, but not in alcohol, of comparatively low dielectric constant (Turner and Pollard, *loc. cit.*).

The point at which, in the dielectric constant scale, molecular association begins to be apparent cannot well be decided because the molecular association depends on the concentration also; but in solutions which are not concentrated, association is clearly in evidence for a number of salts, such as tetrapropylammonium iodide and quinoline ethoiodide in alcohol, and in acetone the indication is still clearer. As the dielectric constant of alcohol is 18 at its boiling point, this value is considered as the one below which molecular association begins to be evident (Turner and Pollard, *loc. cit.*). This was, therefore, another reason which led us to choose ethyl alcohol as one of the solvents, water being chosen on account of its possessing a very high dielectric constant. It was expected that the substituted quaternary azonium iodides would show lower molecular weights in water, but that they would give normal molecular weights in ethyl alcohol. This expectation is not realised experimentally, as the molecular weights are found to be below the normal in ethyl alcohol also. The molecular weights of four out of the five substituted quaternary azonium iodides are lower in ethyl alcohol than in water; phenyldiethylazonium iodide being the only case in which the molecular weight is slightly lower in water than in ethyl alcohol. In other words, the degree of association, in these four cases, is greater in water, a solvent with high dielectric constant ($K_{100°}$ 66) than in ethyl alcohol, which possesses a comparatively low value for the dielectric

[2] J. J. Thomson, *Phil. Mag.*, 1893, (V), **36**, 313; Nernst, *Zeitsch. physikal. Chem.*, 1894, **13**, 535.

[3] Meldrum and Turner, *J.C.S.*, 1908, **93**, 876; 1910, **97**, 1605.

[4] Peddle and Turner, *J.C.S.*, 1911, **99**, 685; Beckmann, *Zeitsch. physikal. Chem.*, 1890, **6**, 437.

constant ($K_{78°}$ 18); in the case of phenyldiethylazonium iodide it is only slightly lower in water (0·74) than in ethyl alcohol (0·78). It is thus clear that the Nernst-Thomson rule is obeyed only in the case of phenyldiethylazonium iodide, but even in this case in no way proportionately to the dielectric constants of the two solvents. It is, however, not followed in the remaining four cases (see Tables I and II). The conclusion which can be drawn from these observations is that the relationship is not so well defined as has been supposed hitherto.

Experimental.

The following five salts were employed in this investigation:—phenyldimethylazonium iodide, phenylmethylethylazonium iodide, phenyldiethylazonium iodide, phenylmethylbenzylazonium iodide and phenylpropylbenzylazonium iodide. They were prepared according to the methods already described by one of us.[5] In each case the salts were purified by five crystallisations from alcohol and ether.

The solvents were specially purified as follows:—

Water.—Distilled water was redistilled in the presence of potassium permanganate and dilute sulphuric acid, the first and last fractions being rejected. It was once more distilled before use.

Ethyl alcohol.—"Absolute alcohol" after being dried over quicklime was fractionally distilled, using a long fractionating column, and the fraction of the correct boiling-point was collected.

The boiling-point determinations were carried out in the form of apparatus as modified by Lumsden-Walker. As, however, the solutions employed were very dilute, the rise in the boiling-point of the solvent was very small, which necessitated the use of the Beckmann thermometer. The inner tube, containing the solution, in the ordinary Lumsden-Walker apparatus, being too small for the introduction of the Beckmann thermometer, a larger tube was prepared from an old piece of another apparatus and was recalibrated in the laboratory. The apparatus was tested with several substances of known molecular weight, and the following typical values obtained with cane sugar are recorded:

Solvent			w	v	Δ	M_v	M_c
Water	..	..	0·2456	9·7	0·04°	341·8	342
,,	..	..	,,	12·9	0·03°	342·7	,,

The molecular elevations of boiling-points (E_w and E_v) used in these calculations are 5°·2 and 5°·4 for water and 11°·5 and 15°·6 for ethyl alcohol. The results of molecular weight determinations are shown in Tables I and II.

[5] Singh, *J.C.S.*, 1913, **103**, 604; 1914, **105**, 1972; 1916, **109**, 780; 1920, **117**, 1203.

TABLE I.

Molecular Weight Determinations in Ethyl Alcohol.

Compound	*w* (solute)	*v*	*s* (solvent)	Δ	M_v	M_w	M_c	%Conc.	100 × degree of association
Phenyldimethylazonium iodide $(C_6H_5)(CH_3)_2(NH_2)$ NI	0·1487	14·5	10·75	0·09°	177·8	176·7	264	1·03	67·1
	0·1632	18·0	13·55	0·08	176·8	173·1	,,	0·91	66·3
	0·1401	19·5	14·60	0·065	172·4	169·8	,,	0·72	64·8
Phenylmethylethylazonium iodide $(C_6H_5)(CH_3)(C_2H_5)(NH_2)$ NI	0·1538	15·5	11·50	0·08	193·5	192·3	278	0·99	69·4
	0·1384	16·0	11·83	0·07	192·8	192·2	,,	0·87	69·2
	0·1435	18·4	..	0·065	187·2	..	,,	0·78	67·3
Phenyldiethylazonium iodide $(C_6H_5)(C_2H_5)_2(NH_2)$ NI	0·1473	13·4	9·85	0·075	228·6	229·3	292	1·1	78·4
	0·1628	16·0	11·85	0·07	226·8	225·7	,,	1·02	77·5
	0·1538	16·5	..	0·064	227·2	..	,,	0·93	77·8
Phenylmethylbenzylazonium iodide $(C_6H_5)(CH_3)(C_7H_7)(NH_2)$ NI	0·1919	14·4	10·80	0·105	198·0	194·6	340	1·33	57·7
	0·1486	15·5	..	0·076	196·8	..	,,	0·96	57·9
	0·1384	16·0	11·83	0·07	192·8	192·2	,,	0·87	56·6
	0·1863	24·8	18·24	0·06	195·3	195·8	,,	0·75	57·5
Phenylpropylbenzylazonium iodide $(C_6H_5)(C_3H_7)(C_7H_7)(NH_2)$ NI	0·1431	14·0	10·33	0·085	187·6	187·4	368	1·02	51·0
	0·1591	19·0	14·02	0·07	186·6	186·4	,,	0·84	50·7
	0·1267	21·5	15·60	0·05	183·9	186·8	,,	0·59	50·4

TABLE II.

Molecular Weight Determinations in Water.

Compound	w (solute)	v	s (solvent)	Δ	M_v	M_w	M_c	%Conc.	100 × degree of association
Phenyldimethylazonium iodide $(C_6H_5)(CH_3)_2(NH_2)NI$	0·1989	12·7	11·82	0·04°	211·4	218·8	264	1·57	81·4
	0·1237	10·6	9·93	0·03	210·1	215·9	,,	1·17	80·7
	0·1108	15·7	14·90	0·018	211·7	214·8	,,	0·71	80·8
Phenylmethylethylazonium iodide $(C_6H_5)(CH_3)(C_2H_5)(NH_2)NI$	0·1861	12·0	11·44	0·04	209·4	211·5	278	1·55	75.7
	0·1458	12·6	11·85	0·03	208·3	213·3	,,	1·16	75·8
	0·0702	9·2	8·73	0·02	206·0	209·1	,,	0·76	74·7
Phenyldiethylazonium iodide $(C_6H_5)(C_2H_5)_2(NH_2)NI$	0·2163	12·0	..	0·045	216·3	..	292	1·80	74·1
	0·1765	11·1	10·51	0·04	214·7	218·3	,,	1·59	74·1
	0·2163	15·2	14·80	0·035	219·6	217·1	,,	1·42	74·8
Phenylmethylbenzylazonium iodide $(C_6H_5)(CH_3)(C_7H_7)(NH_2)NI$	0·2632	12·4	..	0·05	229·2	..	340	2·12	67·4
	0·2632	17·8	16·86	0·035	228·1	231·9	,,	1·48	67·6
	0·1957	15·5	14·81	0·03	227·3	229·0	,,	1·26	67·1
Phenylpropylbenzylazonium iodide $(C_6H_5)(C_3H_7)(C_7H_7)(NH_2)NI$	0·2325	13·2	12·60	0·04	237·8	239·9	368	1·76	64·9
	0·1852	19·9	18·85	0·022	228·4	232·2	,,	0·93	62·7

In the tables, w = weight of the solute in grams;
v = volume of the solution in c.c.;
s = weight of the solvent in grams;
Δ = rise in boiling-point of solvent;
M_v = molecular weight by the volume method;
M_w = molecular weight by the weight method;
M_c = molecular weight calculated from the formula.

The percentage concentration is expressed as the number of grams of the solute in 100 c.c. of the solution. The last column in the tables gives the percentage degree of association expressed as the ratio of the mean of observed molecular weights (M_w and M_v) to the calculated formula weight of the compound.

The molecular weight determinations were carried out by Mr. Sud in 1919 at the Government College, Lahore, and submitted as a thesis in partial fulfilment of the requirements for the M.Sc. degree of the Punjab University.

This work will be extended to these and other substituted quaternary azonium salts, using higher concentrations and other solvents.

Summary.

1. The molecular weights of phenyldimethylazonium, phenylmethylethylazonium, phenylmethylbenzylazonium and phenylpropylbenzylazonium iodides are lower in ethyl alcohol than in water; in the case of phenyldiethylazonium iodide this relation is reversed. The degree of association is, therefore, lower in ethyl alcohol, a solvent of low dielectric constant, than in water, a solvent which has a very high value. It is, therefore, clear that the Nernst-Thomson rule is not followed in these four cases.

2. In aqueous solution, the degree of association of the above-mentioned substituted quaternary azonium iodides decreases with increase in formula weight of the base; but this regularity does not appear to hold in ethyl alcohol.

3. The degree of association of the salts decreases with dilution in both the solvents.

4. The molecular weights furnished by the two methods, namely, the volume and the weight methods, are nearly identical for very dilute solutions.

THE DISTRIBUTION OF THE MEAN OF FISHER'S t^2 FOR SAMPLES FROM A NORMAL POPULATION.

By P. V. Krishna Iyer,

Statistician, Imperial Agricultural Research Institute, New Delhi.

Received April 20, 1937.

(Communicated by Rao Bahadur B. Viswa Nath, F.I.C.)

Introduction.

In 1908, " Student " worked out the distribution of the ratio of the difference between the means of a population and a sample to the standard deviation of the sample. By using this distribution he developed his Z test which is used to see whether two samples belong to the same normal population. This test was established on a more rigorous basis by Fisher in 1925. He also showed how the general effect of the difference between the means of a number of samples can be judged by using the method of the analysis of variance. In the case of two samples it has already been shown that z test and t test are identical. But the exact relation between these two tests when there are more than two samples does not appear to have been studied so far. It is the purpose of the author here to establish the exact relation between Fisher's t and z tests, to determine the distribution of the mean of Fisher's t^2 for samples from a normal population and to suggest some improvements in the methods of analysis followed in the case of data involving several groups with unequal numbers in the different groups.

Relation between Fisher's t *and* z.

Let the means of p treatments replicated n times be given by :—

$$T_1, T_2, T_3, \cdots\cdots, T_p.$$

The variance due to treatments is equal to :

$$\frac{n}{p(p-1)} \left\{ p \sum_{r=1}^{r=p} T_r^2 - \left(\sum_{r=1}^{r=p} T_r \right)^2 \right\}$$

$$= \frac{n}{p(p-1)} \left\{ \sum_{\substack{r,s=1 \\ r \neq s}}^{r,s=p} (T_r - T_s)^2 \right\}$$

$$= \frac{1}{pc_2} \left\{ \sum_{\substack{r,s=1 \\ r \neq s}}^{r,s=p} \frac{n(T_r - T_s)^2}{2} \right\}$$

The ratio of the variances due to treatments and residual error is equal to

$$\frac{1}{p^{c_2} \cdot s_1^2} \left\{ \sum_{\substack{r,\ s=1 \\ r \neq s}}^{r,\ s=p} \frac{n(T_r - T_s)^2}{2} \right\}, \quad s_1^2 \text{ being the residual variance}$$

$$= \frac{1}{p^{c_2}} \left\{ \sum_{\substack{r,\ s=1 \\ r \neq s}}^{r,\ s=p} \frac{n(T_r - T_s)^2}{2 s_1^2} \right\}$$

$$= \frac{1}{p^{c_2}} \left\{ \sum_{r,\ s=1}^{r,\ s=p} t_{rs}^2 \right\} = \bar{t}^2, \text{ where } \bar{t}^2 \text{ is the average of all the } t^2\text{'s that}$$

can be formed.

Distribution of the Mean of a Number of Observed t^2*'s as based on Pooled Variance.*

In the previous section we have seen that $\bar{t}^2 = s_2^2/s_1^2$, where s_2^2 and s_1^2 are the variances due to treatments and residual error. Substituting $\bar{t}^2 = e^{2z} = s_2^2/s_1^2$ in the distribution of z, we find that the distribution of $\bar{t}^2$ is given by

$$\frac{2\, n_1^{\frac{n_1}{2}}\, n_2^{\frac{n_2}{2}}\, \Gamma \frac{n_1+n_2}{2}}{\Gamma \frac{n_1}{2}\ \Gamma \frac{n_2}{2}} \cdot \frac{\bar{t}^{(n_1-1)}\, d\bar{t}}{(n_1 \bar{t}^2 + n_2)^{\frac{n_1+n_2}{2}}}, \text{ where } n_1 \text{ and } n_2 \text{ are the degrees}$$

of freedom of the variances s_2^2 and s_1^2 respectively.

It follows from the above expression that the distribution of $\bar{t}$ is dependent on the degrees of freedom of the error on which comparisons are made and the number of independent t's that can be formed. Further, it can also be shown that if there are m independent t^2's the distribution of the average of all these t^2's is given by

$$\frac{2\, m^{\frac{m}{2}}\, n^{\frac{n}{2}}\, \Gamma \frac{m+n}{2}}{\Gamma \frac{m}{2}\ \Gamma \frac{n}{2}} \cdot \frac{\bar{t}^{(m-1)}\, d\bar{t}}{(m\bar{t}^2 + n)^{\frac{m+n}{2}}} \qquad \text{(A)}$$

n being the degrees of freedom of the variance on the basis of which comparisions are effected.

This distribution of the average of a number of independent t^2's can be established on a more rigorous basis as follows :—

$$m\bar{t}^2 = t_1^2 + t_2^2 + t_3^2 + \cdots t_m^2$$

$$= \frac{1}{s_1^2} \left\{ \frac{(\bar{x}_1 - \bar{y}_1)^2\, n_1 n_1'}{n_1 + n_1'} + \frac{(\bar{x}_2 - \bar{y}_2)^2\, n_2 n_2'}{n_2 + n_2'} + \cdots \frac{(\bar{x}_m - \bar{y}_m)^2\, n_m n_m'}{n_m + n_m'} \right\}$$

$$= \frac{1}{s_1^2} \left\{ s_1'^2 + s_2'^2 + s_3'^2 + \cdots s_m'^2 \right\} = \frac{m\, s_2^2}{s_1^2}$$

$\therefore \quad \bar{t}^2 = s_2^2/s_1^2$, *i.e.*, the ratio of two variances.

It should be noted that s_1^2 is the value of the pooled variance for all the samples and $n_1, n_2 .. n_1' n_2' ....$ are the sizes of the samples.

Therefore the distribution of the mean of m independent t^2's reduces to the distribution of the ratio of two variances and is given by the expression (A).

The advantage of the above finding is that if we have M persons collecting samples from two places the significance between the two places is best judged by finding the significance of the average of the t^2's for the M persons on the basis of the pooled variance. Thus, if the means for the two places as observed by M persons are

$\bar{x}_1, \bar{x}_2, \bar{x}_3, \cdots \cdots \bar{x}_M,$ (size of each sample $= n_1$)

$\bar{y}_1, \bar{y}_2, \bar{y}_3, \cdots \cdots \bar{y}_M,$ (,, ,, $= n_2$)

$$\bar{t}^2 = \frac{n_1 n_2}{(n_1 + n_2)\, M} \left\{ \sum_{r=1}^{r=M} \frac{(\bar{x}_r - \bar{y}_r)^2}{s_1^2} \right\}$$

s^2_1 is the pooled variance of different samples for various localities by the M persons. The significance of observed value of t^2 can be determined by the aid of Snedecor's ' F ' Tables.

Suggestions for improving the Analysis of Samples of different sizes.

So far we have dealt with cases where the frequencies in different groups or samples are the same. The usual procedure when the sizes of the samples are different, is to use an extension of Fisher's analysis of variance. The variance due to treatments is determined by weighting the mean squared differences by the respective sizes.

Variance between groups or treatments is equal to

$$\frac{1}{p-1} \left\{ n_1 (\bar{x}_1 - \bar{x})^2 + n_2 (\bar{x}_2 - \bar{x})^2 + \cdots \cdots n_p (\bar{x}_p - \bar{x})^2 \right\}$$

where $\bar{x}_1, \bar{x}_2, \cdots \bar{x}_p$ are the means of the different groups and $\bar{x}$ is the general mean.

In the above case it will be seen that the ratio of the variances due to treatments and residual error does not, as in the case of samples of equal sizes, reduce to the average of all the t^2's that can be formed. The discussions in the preceding paragraphs suggest that the significance between the different groups can be judged better by taking the average of the t^2's

$$\bar{t}^2 = \frac{1}{p C_2} \left\{ \sum_{r,s=1}^{r,s=p} \frac{(\bar{x}_r - \bar{x}_s)^2 n_r n_s}{(n_r + n_s)\, s_1^2} \right\}$$

Summary.

It has been established that the average of a number of independent t^2's calculated on the basis of a common appropriate variance is equal to the ratio of two variances. By using this fact the distribution of the average of Fisher's t^2 for samples from a normal population has been derived. In view of this finding some suggestions have been put forward for determining the significance of the difference between the means of samples of different sizes.

REFERENCES.

Brandt, A. E., *J. Amer. Stat. Assoc.*, 1933, **28**, 164.

Fisher, R. A., *Metron*, 1925, **5**, 90-104.

———— *Statistical Methods for Research Workers*, 6th Edition, 1936.

Krishna Ayyar, P. V., *Curr. Sci.*, 1937, **5**, 473-474.

Snedecor, G. W., *Calculation and Interpretation of Analysis of Variance and Covariance*, 1934.

" Student," *Biometrika*, 1908, **6**, 1–25.

Yates, F., *J. Amer. Stat. Assoc.*, 1934, **29**, 51-66.

THE MAGNETIC SUSCEPTIBILITY OF COPPER AMALGAM.

By H. S. Venkataramiah.

(*From the Department of Physics, Central College, Bangalore, University of Mysore.*)

Received June 7, 1937.

(Communicated by Prof. B. Venkatesachar, M.A., F.Inst.P.)

In connection with the recent developments in the theory of the magnetism of free electrons in metals, the experimental study of the magnetic properties of binary alloys and amalgams is of considerable interest. Though the alloys have been extensively studied, the investigation of the magnetic properties of amalgams has not received the same amount of attention. Until very recently the papers on the subject were only two, the first by Gnesotto and Binghinotto[1] and the second by Davies and Keeping.[2] Consequently the present work on the measurement of magnetic susceptibility of copper amalgams, which had not so far been studied, was undertaken. During the progress of this work a paper on the magnetic properties of amalgams was published by Bates and Tai[3] who have measured susceptibilities of several amalgams among which copper amalgam is one. They have drawn definite conclusions regarding the properties of the amalgams of all the other metals except that of copper. Hence it is considered necessary to publish this work in which definite data on the magnetic properties of copper amalgams have been obtained.

Preparation of the Amalgam.

The mercury used in the preparation of the amalgam was purified by the following process. It was passed twice through a column of dilute nitric acid in the form of a fine spray, washed and dried. It was next distilled in a pyrex apparatus under reduced pressure. The distillate was redistilled and the process repeated so that the final product was the result of four successive distillations. The amalgam was prepared by electrolysing pure copper sulphate solution having pure mercury as cathode. The amount of copper dissolved in mercury was found by having, throughout, another copper voltameter with a copper cathode in series with the first one and finding the increase in weight of the cathode. The amalgam so prepared was washed, dried and stored in a desiccator until it was taken up for measurement.

Method of Measurement.

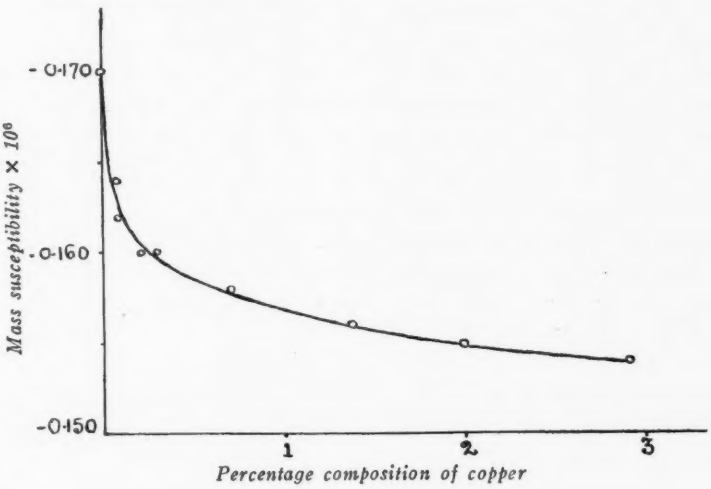
The susceptibilities of mercury and the amalgams were measured by comparison with that of water which was taken as the standard substance,

employing a Curie balance. Correction was applied for the magnetic susceptibility of the air displaced by the substance under investigation.

The susceptibility of one of the amalgams was measured at three different field strengths. Since the value for the susceptibility did not vary, the material under investigation was taken to be free from ferromagnetic impurity.

Experimental Results.

Mass per cent. of copper	Mass susceptibility of amalgam $\times 10^6$ (Observed)	Mass susceptibility of amalgam $\times 10^6$ (Calculated)
0·00	−0·170	−0·170
0·08	−0·164	−0·170
0·10	−0·162	−0·1699
0·22	−0·160	−0·1698
0·30	−0·160	−0·1697
0·70	−0·158	−0·1694
1·39	−0·156	−0·1688
2·00	−0·155	−0·1682
2·92	−0·154	−0·1674



The susceptibility of pure mercury was found to be $-0{\cdot}170 \times 10^{-6}$ and is much lower than the value $-0{\cdot}19 \times 10^{-6}$ given in the *International Critical Tables*, but it agrees with the recent value $-0{\cdot}168 \times 10^{-6}$ obtained by Bates and Tai[3] and Vogt.[4] In the light of these results it may be concluded that the value for the mass susceptibility of mercury accepted so far is inaccurate and must be revised.

The values of the mass susceptibilities of the amalgams obtained in this investigation are entered in the second column of the table against the mass composition of copper in the amalgam entered in the first column. The values which are calculated by the application of the mixture law assuming the mass susceptibility of copper to be $-0{\cdot}082 \times 10^{-6}$ are given in the third column. It is found that the diamagnetic susceptibility of the amalgam is less than that calculated according to the mixture law. The values of the mass susceptibility are plotted against mass composition and the resulting curve shows that the values do not obey the linear law. It may be concluded from these results that addition of even small quantities of copper decreases the diamagnetic susceptibility of mercury considerably.

Discussion.

In general the susceptibility of a liquid or solid metal on admixture with small quantities of foreign metals, deviates from the value deduced according to the mixture law in the direction of greater diamagnetism. It has also been found that the electrical conductivity of the metal is at the same time brought down by such admixtures. These changes may be traced to a common cause, the decrease in the effective number of free electrons. The case of mercury is exceptional as revealed in the present work and those of the other workers. The diamagnetism of the amalgams including that of copper is less than the value obtained from the additivity relation. Hence on amalgamation the effective number of free electron must increase. That such an increase occurs is supported by the fact that the electrical conductivity of mercury is increased by the presence of foreign metals in it.

REFERENCES.

1. *International Critical Tables*, 1926, **6**, 365.
2. Davies, W. G., and Keeping, E. S., *Phil. Mag.*, 1929, **7**, 145.
3. *Proc. Phys. Soc.*, 1936, **48**, 795.
4. *Ann. Phys. Lpz.*, 1932, **14**, 1 and 1935, **21**, 791.

CHEMISTRY OF β-ARYL GLUTACONIC ACIDS.

Part III. Condensations with Phenolic Ethers (*Continued*).

By G. R. Gogte, M.Sc., Ph.D.

(*From the Department of Organic Chemistry, Indian Institute of Science, Bangalore.*)

Received May 21, 1937.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

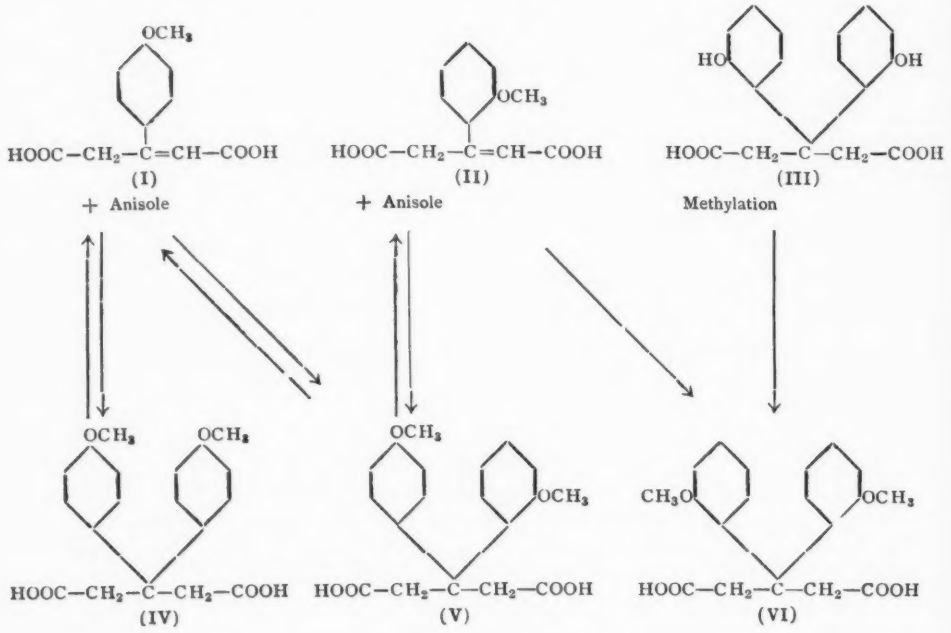
Introduction.

In Part II of this series[1] a phenolic ether—*p*-cresol-ethylether—has been shown to add on to the double bond in a β-aryl-glutaconic acid to produce a ββ-diaryl-glutaconic acid. Dixit and Gokhale[2] have recently described the formation of a similar ββ-diaryl-glutaric acid in the condensation of phenol with acetone-dicarboxylic acid. In view of the stability of their compound, the structure (III) proposed by the authors seems to be untenable as such a compound would immediately lose water to form a neutral dilactone. Moreover, the condensation of dimethyl-oxalate or dimethyl-phthalate with the dimethyl ester of the glutaric acid, described by the authors to proceed in the Claisen's manner in comparison with the ββ-dimethyl-glutaric acid,[3] is quite unlikely, since the two free phenolic hydroxyls in the glutaric ester would first react with the sodium methoxide or sodium, thus inhibiting the reaction to proceed in the manner suggested. In view of this, it was thought desirable to see whether light could be thrown on the real nature of the compound in question by relating it to any of the glutaconic acids containing phenol or anisole in the β-position.

On carrying out the condensation of phenol with acetone-dicarboxylic acid under the conditions of Dixit and Gokhale,[2] a dicarboxylic acid, m.p. 235° C. (decomp.), has now been obtained, but this appears to be different from the one described by the authors, in that it does not give even a trace of the coumarin-4-acetic acid,[4] by the action of sulphuric acid, and that it did not produce any anhydride on thermal decomposition as the authors claimed to have observed, but lost carbon dioxide instead. On trying to synthesise the dicarboxylic acid, m.p. 235° C., from the known

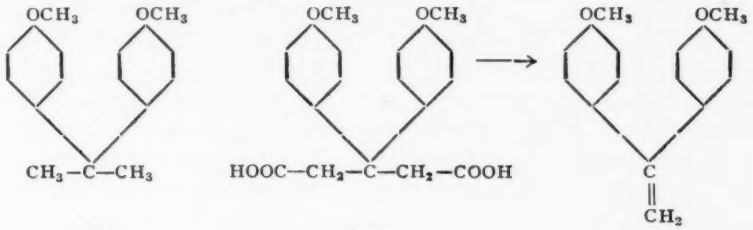
[1] Gogte, *Proc. Ind. Acad. Sci.*, (A), 1935, **1**, 185–198.
[2] Dixit and Gokhale, *J. Uni. Bombay*, 1934, **3**, 80–94.
[3] Dieckmann, *Ber.*, **32**, 1230 ; Komppa, *Annalen*, **368**, 126.
[4] Limaye, *J. Ind. Chem. Soc.*, 1927, **4**, 159.

β-4-hydroxy-phenyl-glutaconic acid,[5] by condensing it with phenol (compare Part II)[1] nothing could be obtained, the glutaconic acid itself having been decomposed apparently by sulphuric acid. Presuming this instability to be due to the presence of a phenolic hydroxyl in the glutaconic acid, it was proposed to see whether the dimethoxy derivative, m.p. 158° C., of the acid m.p. 235° C. could be related by synthesis from or degradation to the β-4-methoxy-phenyl-glutaconic acid (I)[6] or the β-2-methoxy-phenyl-glutaconic acid (II), which was easily synthesised from the known coumarin-4-acetic acid[4] by hydrolysis and methylation.[7] It was observed that the latter (II) could not be made to condense with anisole at all, whereas the former (I) easily condensed with anisole to produce the dimethoxy acid, m.p. 158° C. Out of the two possible structures (IV) and (V) arising out of this synthesis, the former is the more probable as the compound lost a molecule of anisole by the action of sulphuric acid to give only the β-4-methoxy-phenyl-glutaconic acid (I). A compound of the structure (V) under these circumstances would have produced a monolactonic acid and the coumarin-4-acetic acid[4] in addition.



[5] Dixit, *J. Ind. Chem. Soc.*, 1931, **8**, 787.
[6] Limaye and Bhave, *J. Ind. Chem. Soc.*, 1931, **8**, 137.
[7] *Cf.* Part I, *Proc. Ind. Acad. Sci.*, (A), 1934, **1**, 48–60.

To further confirm the constitution (IV) it was decided to see whether the dimethoxy acid, m.p. 158° C. could be decarboxylated to the known ββ-di-(4-methoxy-phenyl) propane (VII), m.p. 60°·5 C.[8] Dilute acids in this respect had no action on the dimethoxy acid, whereas thermal decomposition yielded its anhydride, m.p. 105°C. On heating the dimethoxy acid with lime, however, a compound melting at 140° C. and differing vastly from the expected one, was obtained. Its emperical formula ($C_{16}H_{16}O_2$) showed a loss of a molecule of acetic acid in addition to one of carbon dioxide during decarboxylation, and it was found identical with the known *unsym.* di-4-methoxyphenyl-ethylene (VIII).[9] This established conclusively the correctness of the structure (IV) for the dimethoxy acid and in consequence of the acid, m.p. 235° C. The elimination of acetic acid in the decarboxylation of organic acids is remarkable, and this along with other similar cases will be described in a separate communication.



(VII) (IV) (VIII)

The glutaconic acids containing phenetole or *o*-cresol-methyl and ethyl ethers in the β-position have been found to condense similarly with the respective phenolic ethers, and the resulting ββ-diaryl-glutaric acids have been found to yield, when heated with lime, the corresponding αα-diaryl-ethylenes, which in the case of phenetole is known.[9] All these ββ-diaryl-glutaric acids could be obtained directly by condensing acetone-dicarboxylic acid with phenolic ethers in the presence of dilute sulphuric acid. No ββ-diaryl-glutaric acid could however be obtained from meta-cresol ethers by any of these reactions. The extension of this reaction to other phenolic ethers is in progress.

Experimental.

Condensation of phenol with acetone-dicarboxylic acid: Formation of ββ-(4 : 4′-dihydroxy-diphenyl)-glutaric acid.—An acetone-dicarboxylic acid sulphuric acid mixture prepared as usual from citric acid (50 g.) and conc. sulphuric acid (80 c.c.) was cooled in a freezing mixture and powdered ice

[8] Dianin, *Br. Chem. Abst.*, **64**, I, 214.
[9] Gattermann, *Ber.*, **22**, 1132.

(20 g.) was cautiously added, not allowing the temperature of the mixture to go above 20° C. It was further cooled to a temperature below 0° C. and phenol crystals (40 g.) were added in small portions with repeated shaking. The reaction mixture was kept at the room temperature for 20 hours and then poured on cursched ice (250 g.). The precipitate which separated after scratching and keeping overnight was filtered, dissolved in sodium carbonate solution and acidified—(16 g.). This was treated with 100 c.c. of boiling water and filtered. The insoluble portion—(3·3 g.), crystallised from alcohol in colourless silky needles, m.p. 184° C. (decomp.), and was identified as the unsubstituted coumarin-4-acetic acid by its decarboxylation to the known 4-methyl-coumarin. (Found : Eq. = 204 ; C = 64·52 per cent. ; H = 3·81 per cent. ; $C_{11}H_8O_4$ requires Eq. = 204 ; C = 64·7 per cent. ; H = 3·92 per cent.)* From the aqueous filtrates the glutaric acid separated on cooling and scratching, which was recrystallised from water (charcoal) in colourless hexagonal plates, m.p. 235° C. (decomp.), (12 g.). (Found : Eq. = 158 ; C = 64·32 per cent. ; H = 4·95 per cent. ; $C_{17}H_{16}O_6$ requires Eq. = 158 ; C = 64·56 per cent. ; H = 5·06 per cent.) The compound is very soluble in alcohol, acetic acid, and acetone, sparingly so in water and ether and insoluble in petrol, benzene and chloroform. It gives dark green colouration with ferric chloride and lost carbon dioxide at its melting point leaving behind a residue which did not melt but charred on further heating.

The *diethyl-ester* of the above crystallised from 30 per cent. methyl alcohol in colourless flat needles, m.p. 158–159° C. (Found : C = 67·58 per cent. ; H = 6·33 per cent. ; $C_{21}H_{24}O_6$ requires C = 67·74 per cent. ; H = 6·45 per cent.) The *dimethyl-ester* crystallised from methyl alcohol in colourless plates, m.p. 189° C. (Found : C = 66·02 per cent. ; H = 5·7 per cent. ; $C_{19}H_{20}O_6$ requires C = 66·28 per cent. ; H = 5·81 per cent.) *ββ-(4 : 4′-diacetoxy-diphenyl)-glutaric anhydride* was obtained by refluxing together the glutaric acid (5 g.), fused sodium acetate (7 g.) and acetic anhydride (12 c.c.) for ½ hour. It crystallised from glacial acetic acid in stout colourless needles, m.p. 204–205° C. (Found : C = 65·8 per cent. ; H = 4·6 per cent. ; $C_{21}H_{18}O_7$ requiries C = 65·96 per cent. ; H = 4·7 per cent.) *ββ′-(4 : 4′-diacetoxy-diphenyl)-glutaric acid*, obtained by refluxing the above

* The coumarin-4-acetic acid, m. p. 172° C. (decomp.), prepared according to Limaye's method (*J. Ind. Chem. Soc.*, 1927, 4, 159) when crystallised from alcohol melted at 184° C. (decomp.) and was found identical with the above one. This thus appears to be the most simple method for the preparation of the unsubstituted coumarin-4-acetic acid, Limaye's method being tedious, requires large quantities of ether, and does not give concordant yields.

anhydride with water, crystallised from water in colourless parallelogramic plates, m.p. 188–189° C. (decomp.). (Found : C = 62·8 per cent. ; H = 4·91 per cent. ; Eq. = 197 ; $C_{21}H_{20}O_8$ requires C = 63·0 per cent. ; H = 5·00 per cent. ; Eq. = 200.) *Diethyl-ββ-(4 : 4′-diacetoxy-diphenyl)-glutarate*, prepared from the above diethyl-ester, sodium acetate and acetic anhydride, crystallised from alcohol in colourless silky needles, m.p. 135° C. (Found : C = 65·58 per cent. ; H = 6·0 per cent. ; $C_{25}H_{28}O_8$ requires C = 65·8 per cent. ; H = 6·1 per cent.)

ββ-(4 : 4′-dimethoxy-diphenyl)-glutaric acid.—The dihydroxy-diphenyl-glutaric acid (5 g.), was methylated by dimethyl-sulphate (25 c.c.) and 25 per cent. sodium hydroxide solution (80 c.c.), on a boiling water-bath. The dimethoxy acid coming out as a sticky semi-solid mass on acidification was treated with 250 c.c. of boiling water and filtered, when it came out in colourless silky needles. When recrystallised from water it melted at 158° C. (Found : Eq. = 171·8 ; C = 66·17 per cent. ; H = 5·74 per cent. ; $C_{19}H_{20}O_6$ requires Eq. = 172 ; C = 66·28 per cent. ; H = 5·81 per cent.) *ββ-(4 : 4′-dimethoxy-diphenyl)-glutaric anhydride* was obtained by heating the dimethoxy acid at 200° C. for 1½ hours till the water evolution stopped. The residue was dissolved in boiling benzene, and the undecomposed dimethoxy acid which separated on cooling was filtered out. On removing the benzene from the filtrate the anhydride remained as an oil which solidified on keeping overnight in a vacuum desiccator over paraffin. It was washed with sodium carbonate and crystallised from methyl alcohol in colourless plates, m.p. 104–105° C. (Found : C = 69·78 per cent. ; H = 5·44 per cent. ; $C_{19}H_{18}O_5$ requires C = 69·94 per cent. ; H = 5·52 per cent). The *semi-anilide* was prepared by heating the above anhydride with aniline in benzene solution. The product separated on cooling in ice and scratching and was crystallised from methyl alcohol in colourless light plates, m.p. 187° C. (Found : C = 71·38 per cent. ; H = 5·82 per cent. ; $C_{25}H_{25}O_5N$ requires C = 71·6 per cent. ; H = 5·96 per cent.)

Synthesis of the ββ-(4 : 4′-dimethoxy-diphenyl)-glutaric acid by the condensation of β-(4-methoxy-phenyl)-glutaconic acid with anisole.—The glutaconic acid (5 g.) was dissolved in ice-cold 75 per cent. aqueous sulphuric acid (60 c.c.) and anisole (8 c.c.) was added in small portions with repeated shaking. The reaction mixture was allowed to remain overnight at the room temperature and poured over crushed ice (100 g.) when a precipitate separated on scratching and keeping overnight. It was filtered, dissolved in sodium carbonate solution, washed with ether, and the dimethoxy acid precipitated by acids. On crystallising from boiling water it melted at 158° C. and was identified by mixed m.p.

Degradation of the ββ-(4 : 4′-dimethoxy-diphenyl)-glutaric acid to the β-(4-methoxy-phenyl)-glutaconic acid.—The glutaric acid (10 g.) was dissolved in 80 per cent. sulphuric acid (50 c.c.) with slight warming, and the solution on keeping for 4 hours was poured in 150 c.c. water, when a product crystallised out on cooling in ice, scratching and keeping overnight (yield 2·5 g.). It was filtered, washed, neutralised by alkali, an excess of barium acetate solution added, and the whole boiled, when a heavy precipitate of a barium salt separated, from which the glutaconic acid was obtained by acidification. It crystalliesd from 50 c.c. of boiling water in colourless needles, m.p. 176° C. (decomp.).

Decarboxylation of the ββ-(4 : 4′-dimethoxy-diphenyl)-glutaric acid to the αα-(4 : 4′-dimethoxy-diphenyl)-ethylene.—The dimethoxy glutaric acid (1 g.) was intimately mixed with freshly ignited lime (3 g.) and placed in a hard glass test-tube supported horizontally. It was cautiously heated by a smoky flame when a red oil collected in the cooler part of the tube. On keeping at the room temperature for a few hours, the oil solidified to a yellow crystalline mass, which was scraped out, washed with methyl alcohol, and crystallised from 50 c.c. of the same solvent in colourless shining leaflets, m.p. 140° C. (0·4 g.), and was identified as the diphenyl-ethylene by mixed m.p. (Found : C = 79·9 per cent. ; H = 6·6 per cent. ; $C_{16}H_{16}O_2$ requires C = 80 per cent. ; H = 6·67 per cent.)

Condensation of anisole with acetone-dicarboxylic acid : Formation of the ββ-(4 : 4′-dimethoxy-diphenyl)-glutaric acid.—An acetone dicarboxylic acid sulphuric acid mixture from citric acid (100 g.), sulphuric acid (160 c.c.) was diluted in cold by ice (40 g.). The whole was cooled to 0° C. and anisole (40 c.c.) was gradually added with shaking. On continuing the shaking for 2 hours, the two layers disappeared, and the reaction mixture on keeping at the room temperature for 24 hours was poured over powdered ice (500 g.), when on scratching and keeping overnight, a precipitate separated. It was filtered, dissolved in sodium carbonate solution, excess of anisole washed out with ether, and represcipitated by acids. The precipitated acids were neutralised exactly with alkalis, the solution boiled with animal charcoal, filtered, and treated with barium acetate solution in small portions, until there was no formation of any precipitate on boiling. The acids precipitated from these filtrates by mineral acids, were filtered and treated with 1·5 liters of boiling water and filtered, when the dimethoxy acid crystallised out in colourless silky needles, m.p. 158 °C. Yield 18 g.

β-(4-ethoxy-phenyl)-glutaconic acid, prepared by condensing phenetole with acetone-dicarboxylic acid, crystallised from methyl alcohol in colourless parallelogramic plates, m.p. 170 °C. (decomp.). (Found : Eq. = 125 ;

C = 62·22 per cent.; H = 5·5 per cent.; $C_{13}H_{14}O_5$ requires Eq. = 125; C = 62·4 per cent.; H = 5·6 per cent.) *Hydroxy-anhydride*, colourless silky needles from benzene, m.p. 178° C. *Semianilide*, colourless light needles from alcohol, m.p. 180° C. (decomp.).

ββ-(4 : 4'-diethoxy-diphenyl)-glutaric acid, was prepared by condensing the above glutaconic acid with phenetole in the usual manner, or by ethylating the *ββ*-(4 : 4'-dihydroxy-diphenyl)-glutaric acid. It crystallised from water in colourless parallelogramic plates, m.p. 157–158° C. (Found : Eq. = 186; C = 66·1 per cent.; H = 6·34 per cent; $C_{21}H_{24}O_6$ requires Eq. = 186; C = 67·4 per cent.; H = 6·45 per cent.) The *anhydride* prepared by decomposing the glutaric acid at 200° C. as usual crystallised from methyl alcohol in colourless glistening plates, m.p. 119–120° C. (Found : C = 70·98 per cent.; H = 6·12 per cent.; $C_{21}H_{22}O_5$ requires C = 71·18 per cent.; H = 6·21 per cent.). The glutaric acid, on decarboxylation with lime yielded the known *αα*-(4 : 4'-diethoxy-diphenyl)-ethylene, which crystallised from methyl alcohol in glistening plates, m.p. 142° C.[10]

Condensation of β-(4-methoxy-3-methyl-phenyl)-glutaconic acid with o-cresol-methyl ether : Formation of the ββ-(4 : 4'-dimethoxy-3 : 3'-dimethyl-diphenyl)-glutaric acid.—The glutaconic acid (5 g.) was condensed with *o*-cresol-methyl ether (8 c.c.) in the presence of ice-cold 80 per cent. sulphuric acid (50 c.c.) as usual. The sticky condensation product was dissolved in dilute sodium carbonate solution, washed with ether and precipitated by acids. The sticky precipitate became granular by refluxing with water, filtered, dried, dissolved in benzene and precipitated by petroleum ether. The glutaric acid thus separated was finally recrystallised from benzene in microscopic colourless flat needles, m.p. 187° C. This glutaric acid gives an insoluble barium salt in cold. (Found : Eq. = 188; C = 67·65 per cent.; H = 6·36 per cent.; $C_{21}H_{24}O_6$ requires Eq. = 186; C = 67·74 per cent.; H = 6·45 per cent.) The *anhydride* was prepared by thermal decomposition of the above glutaric acid as usual. The sticky mass solidified by rubbing with ether and crystallised from alcohol in colourless parallelogramic plates, m.p. 156° C. (Found : C = 71·07 per cent.; H = 6·14 per cent.; $C_{21}H_{22}O_5$ requires C = 71·18 per cent.; H = 6·21 per cent.) The *semianilide* prepared from the above anhydride and aniline in benzene solution, precipitated by cooling in ice and adding petroleum ether. It was filtered, refluxed with 30 per cent. methyl alcohol and crystallised from methyl alcohol in colourless parallelogramic plates, m.p. 189° C. (Found : C = 72·28 per cent.; H = 6·35 per cent.; $C_{27}H_{29}O_5N$ requires C = 72·48 per cent.; H = 6·48 per cent.)

[10] Gattermann, *Ber.*, **22**, 1132.

The above glutaric acid was degraded to the known β-(4-methoxy-3-methyl-phenyl)-glutaconic acid[11] by the action of 80 per cent. sulphuric acid as usual. The glutaconic acid was separated from the unreacted glutaric acid by its insolubility in benzene. It was crystallised from 5 per cent. acetic acid, m.p. 173° C. (decomp.). The glutaric acid was decarboxylated by heating with lime as usual to the αα-(4 : 4′-dimethoxy-3 : 3′-dimethyl-diphenyl)-ethylene, which crystallised from methyl alcohol in colourless light glistening plates, m.p. 106° C. (Found : C = 80·36 per cent. ; H = 7·32 per cent. ; $C_{18}H_{20}O_2$ requires C = 80·6 per cent. ; H = 7·46 per cent.) The glutaric acid could also be synthesised by condensing the acetonedicarboxylic acid sulphuric mixture from citric acid (25 g.), sulphuric acid (40 c.c.)—diluted with addition of ice (10 g.), with *o*-cresol-methyl ether (10 c.c.) in the usual manner. Yield 8 g.

β-(4-ethoxy-3-methyl-phenyl)-glutaconic acid crystallised from 40 per cent. methyl alcohol in yellowish microscopic needles, m.p. 174° C. (decomp.). The *hydroxy-anhydride* crystallised from benzene in colourless plates, m.p. 188° C. The *semianilide* crystallised from alcohol in colourless silky needles, m.p. 173°C.

ββ-(4 : 4′-diethoxy-3 : 3′-dimethyl-diphenyl)-glutaric acid was prepared by condensing the above glutaconic acid with *o*-cresol-ethylether in the usual manner. The sticky product was refluxed with water and crystallised from alcohol in colourless parallelogramic plates, m.p. 204° C. (decomp.). The glutaric acid gives insoluble barium salt. (Found : Eq. = 203 ; C = 68·89 per cent. ; H = 6·92 per cent. ; $C_{23}H_{28}O_6$ requires Eq. =200 ; C =69 per cent. ; H = 7 per cent.) The *anhydride* prepared by thermal decomposition at 210–220° C. crystallised from methyl alcohol in colourless glistening light plates, m.p. 104–105° C. The *semianilide* prepared from the above anhydride and aniline in benzene solution was digested with 20 per cent. methyl alcohol, and crystallised from 75 per cent. methyl alcohol in colourless rectangular plates, m.p. 155–156° C.

The glutaric acid was decarboxylated by heating with lime as usual to the αα-(4 : 4′-diethoxy-3 : 3′-dimethyl-diphenyl)-ethylene, which crystallised from methyl alcohol in light flat needles, m.p. 95–96° C. (Found : C = 80·83 per cent. ; H = 8·0 per cent. ; $C_{20}H_{24}O_2$ requires C = 81·08 per cent. ; H = 8·1 per cent.) The glutaric acid could also be prepared by condensing *o*-cresol-ethylether directly with acetone-dicarboxylic acid sulphuric acid mixture diluted with ice as usual.

The author wishes to express his thanks to Dr. P. C. Guha, D.Sc., for the encouragement given and the facilities provided while carrying on the present investigation.

[11] Dixit, *J. Ind. Chem. Soc.*, 1931, **8**, 787.

HETEROCYCLIC COMPOUNDS.

Part II. The Synthesis of Cyclopenteno-(1' : 2' : 4 : 3)-carbostyril Derivatives.

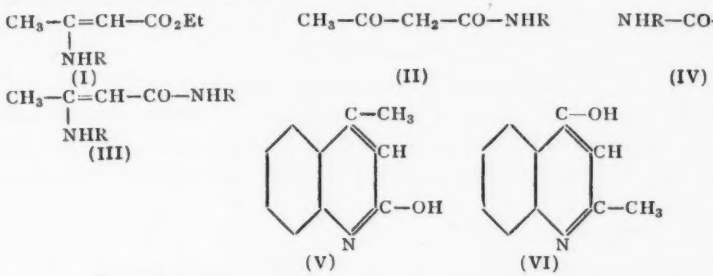
By S. Zafaruddin Ahmad and R. D. Desai.

(From the Department of Physics, Muslim University, Aligarh.)

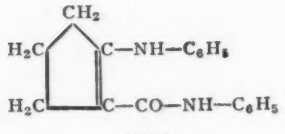
Received April 9, 1937.

(Communicated by Dr. R. K. Asundi, M.Sc., Ph.D.)

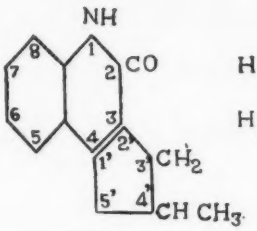
The condensation of arylamines with open-chain β-ketonic esters has been the subject of an extensive study by various investigators.[1] The reaction is an exceedingly complex one, but the following six types of compounds have been definitely isolated according to the experimental conditions. Thus ethyl acetoacetate and a primary arylamine give ethyl β-arylamino-crotonate (I), acetoacetarylamide (II), β-arylamino-crotonoarylamide (III), Sym-diarylurea (IV), substituted 2-hydroxy-lepidine (V), and substituted 4-hydroxy-quinaldine (VI).



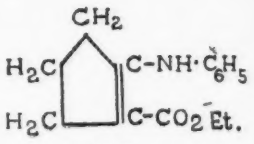
On the other hand, the work on the condensation of these amines with cyclic β-ketonic esters is very meagre. Dieckmann[2] has studied the action of aniline on 4-methylcyclopentanone-2-carboxylate, obtaining 1-anilino-Δ 1 : 2-4-methylcyclopentene-2-carboxyanilide (VII) which was cyclised to 4'-methylcyclopenteno-(1' : 2' : 4 : 3)-carbostyril (VIII). Blount, Perkin and Plant[3] succeeded in condensing cyclopentanone-2-carboxylate with aniline with the formation of 1-anilino-Δ 1 : 2-cyclopentene-2-carboxylate (IX) and cyclopentanone-2-carboxyanilide (X) which were easily cyclised to 4-keto-1 : 4 dihydro-cyclopenteno-(1' : 2' : 2 : 3)-quinoline (XI) and cyclopenteno-(1' : 2' : 4 : 3)-carbostyril or 2-keto-1 : 2 dihydro-cyclopenteno-(1' : 2' : 4 : 3)-quinoline (XII) respectively.



(VII)

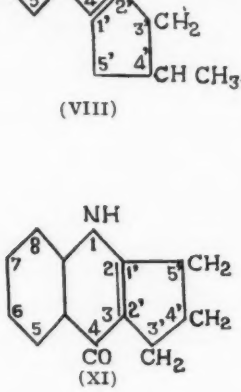


(VIII)

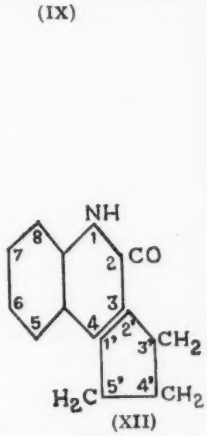


(IX)

(X)

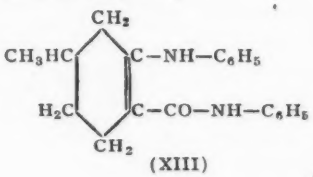


(XI)

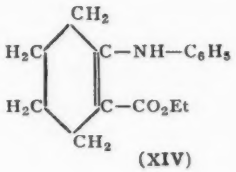


(XII)

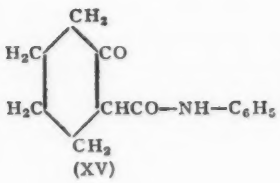
Kötz and Merkel[4] obtained 1-anilino-Δ 1 : 2-5-methyl-cyclohexene-2-carboxyanilide (XIII) from aniline and 5-methylcyclohexanone-2-carboxylate, while Sen and Basu[5] have studied the condensation of cyclohexanone-2-carboxylate with various aromatic amines isolating 1-anilino-Δ 1 : 2-cyclohexene-2-carboxylate (XIV) and cyclohexanone-2-carboxyanilide (XV), and Sym-diarylureas (IV). They also succeeded in cyclising (XIV) and (XV) into their respective tetra-hydro-acridones (XVI) and tetra-hydro-phenanthridones (XVII).



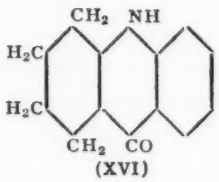
(XIII)



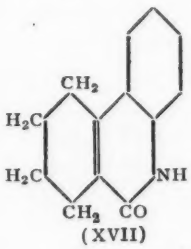
(XIV)



(XV)



(XVI)



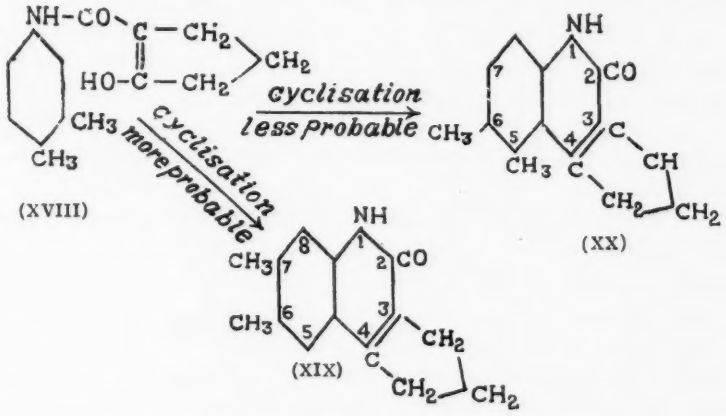
(XVII)

There being a considerable lacuna in the work on the condensation of aromatic amines with cyclopentanone-2-carboxylate, we studied the action of aniline, *p*-toluidine, 1 : 3 : 4-xylidine, α-naphthylamine, β-naphthylamine, *p*-chloraniline, *p*-bromaniline, and *o*-anisidine on this ester by heating at 170–180° for a period varying from two to five minutes using equimolecular quantities. The first three amines gave a mixture, separable into products of type (X) and (VII) while others gave compounds exclusively of the type (VII). The arylamides of type (X) were smoothly cyclised into the carbostyril derivatives of type (XII) by concentrated sulphuric acid, while contrary to the observation of Dieckmann (*loc. cit.*), the compounds of the type (VII) could not be cyclised.

4-Methylcyclopentanone-2-carboxylate was condensed with aniline, *p*-toluidine, 1 : 3 : 4-xylidine, *p*-chloraniline, and *p*-bromaniline under identical conditions. Aniline and *p*-toluidine gave compounds of type (X) but although pure, crystalline products could not be isolated, the crude products were smoothly converted into carbostyril derivatives. 1 : 3 : 4-xylidine gave a separable mixture of products of types (X and VII) while *p*-chloraniline and *p*-bromaniline gave products of type (VII) only.

The 1 : 3 : 4-xylidides (XVIII) obtained from the two esters may cyclise giving either, 6 : 7-dimethyl- (IXX) or 5 : 6-dimethyl-derivative (XX) of carbostyril, but as the possibility for the former is much greater, we have assumed that they are 6 : 7-dimethyl-derivatives (IXX).

When the reaction was carried out at the boiling point of the mixture, only Sym-diarylureas could be isolated in a pure condition, showing that compounds of types (VII) and (X) underwent decomposition to Sym-diarylureas. We are busy studying the action of arylamines on these as well as



other cyclic β-ketonic esters to standardise conditions for the individual isolation of compounds of type (VII, IX and X) in each reaction.

Experimental.

Cyclopentanone-2-carboxyanilide (type X).—A mixture of cyclopentanone-2-carboxylate (1·5 g.) and aniline (1·5 g.) was heated at 155–160° in an oil-bath for five minutes. The solid that separated out after 24 hours was collected, washed with petrol (b.p. 60–80°) and crystallised from alcohol, when colourless needles, m.p. 105–106°, were obtained. Its alcoholic solution gave a dark green colour with ferric chloride. On heating it with concentrated sulphuric acid on a water-bath for 15–20 minutes, and pouring the cooled mixture into water, a solid was formed which crystallised from dilute acetic acid in colourless plates, m.p. 256°. This was, therefore, *cyclopenteno-*(1' : 2' : 4 : 3)*-carbostyril* (XII) [*cf.* Blount, Perkin and Plant (*loc. cit.*)].

*Cyclopentanone-2-carboxy-*p*-toluidide (type X).*—A mixture of the ester (2.5 g.) and *p*-toluidine (1·7 g.) was heated in an oil-bath at 180° for two minutes. The solid (m.p. 105–110°) which separted on rubbing the cold mixture with petrol (b.p. 60–80°), was separated, washed, and treated with cold alcohol, which dissolved only a part of the solid. On concentration, the alcoholic solution gave colourless needles, m.p. 130°. Its alcoholic solution gave violet colour with ferric chloride. (Found : C, 72·0 ; H, 7·3 ; $C_{13}H_{15}O_2N$ requires C, 71·9 ; H, 6·9 per cent.)

1-p-*Tolylamino-*Δ 1 : 2-*cyclopentene-2-carboxy-*p*-toluidide (type VII).*—The residue insoluble in cold alcohol dissolved on warming, and crystallised on cooling in colourless needles, m.p. 143°. Its alcoholic solution did not give any colour with ferric chloride. (Found : C, 78·9 ; H, 7·5 ; $C_{20}H_{22}O\,N_2$ requires C, 78·4 ; H, 7·2 per cent.) Its solution in concentrated sulphuric acid did not cyclise on warming.

6-*Methyl-2-keto-*1 : 2-*dihydro-cyclopenteno-*(1' : 2' : 4 : 3)*-quinoline (type XII).*—The solution of cyclopentanone-2-carboxy-*p*-toluidide (0·5 g.) in concentrated sulphuric acid (10 c.c.) was heated on a water-bath for 15 minutes. The solid which was obtained on pouring the cooled mixture into water was collected, washed and crystallised from alcohol when colourless needles, m.p. 295°, were obtained. (Found : C, 78·3 ; H, 6·8 ; $C_{13}H_{13}ON$ requires C, 78·4 ; H, 6·5 per cent.)

Cyclopentanone-2-carboxy-(1 : 3 : 4)*-xylidide.*—A mixture of the ester (2 g.) and 1 : 3 : 4-xylidine (1.6 g.) is heated in an oil-bath at 180–185° for three minutes. The solid that separated out by rubbing the cooled mixture with petrol (b.p. 60–80°) was filtered off, and washed with the same solvent.

The residue (m.p. 110–150°) was treated with cold alcohol, and on concentration, a solid was obtained. This crystallised from petrol in needles or from dilute alcohol in plates, m.p. 107–108°. Its alcoholic solution gave a dark-green colour with ferric chloride. (Found : C, 72·4 ; H, 7·3 ; $C_{14}H_{17}O_2N$ requires C, 72·7 ; H, 7·4 per cent.)

1-*Xylidino*-(1 : 3 : 4)-Δ 1 : 2-*cyclopentene*-2-*carboxy*-(1 : 3 : 4)-*xylidide.*—The residue insoluble in alcohol dissolved on warming, and crystallised from the same solvent on cooling in colourless needles, m.p. 184°. Its alcoholic solution did not give any colouration with ferric chloride, nor did it undergo cyclisation on heating with concentrated sulphuric acid. (Found : C, 78.9 ; H, 8·0 ; $C_{22}H_{26}ON_2$ requires C, 79·0 ; H, 7·8 per cent.)

6 : 7-*Dimethyl*-2-*keto*-1 : 2-*dihydro-cyclopenteno*-(1' : 2' : 4 : 3)-*quinoline.*—The solution of cyclopentanone-2-carboxy-(1 : 3 : 4)-xylidide (0·5 g.) in concentrated sulphuric acid (10 c.c.) was heated in a boiling water-bath for 15 minutes. The flocculent precipitate obtained by pouring into a large volume of water, was filtered, washed and crystallised from methyl alcohol, when colourless needles, m.p. 280°, were obtained. (Found : C, 78·6 ; H, 7·0 ; $C_{14}H_{13}ON$ requires C, 78·9 ; H, 7·0 per cent.)

1-p-*Chloranilino*-Δ 1 : 2-*cyclopentene*-2-*carboxy*-p-*chloranilide.*—The mixture of the ester (2·5 g.) and *p*-chloranilide (2·2 g.) was heated in an oil-bath at 180–185° for three minutes. After treating the cooled mass with petrol, the residue was crystallised from warm alcohol, when colourless needles, m.p. 173–174°, were obtained. Its alcoholic solution did not give any colour with ferric chloride, and the substance could not be cyclised by the usual method. (Found : Cl, 20·3 ; $C_{18}H_{16}N_2OCl_2$ requires Cl, 20·5 per cent.)

1-p-*Bromanilino*-Δ 1 : 2-*cyclopentene*-2-*carboxy*-p-*bromanilide.*—This was similarly prepared from the ester (2 g.) and *p*-bromaniline (1·8 g.) and crystallised from dilute, warm alcohol in colourless needles, m.p. 179°. It resembled the chloro-analogue in its chemical properties. (Found : Br, 36·4 ; $C_{18}H_{16}ON_2Br_2$ requires Br, 36·7 per cent.)

1-o-*Anisidino*-Δ 1 : 2-*cyclopentene*-2-*carboxy*-o-*anisidide.*—A mixture of *o*-anisidine (2 g.) and the ester (2 g.) was heated for 5 minutes at 150°. After washing the solid with petrol, the residue crycstallised from warm, dilute alcohol in colourless plates m.p. 130–131°. Its alcoholic solution gave no colour with ferric chloride, and no cylisation was possible by warming it with concentrated sulphuric acid. (Found : C, 70·8 ; H, 6·4 ; $C_{20}H_{22}O_3N_2$ requires C, 71·0 ; H, 6·5 per cent.)

1-α-*Naphthylamino*-Δ 1: 2-*cyclopentene*-2-*carboxy*-α-*naphthalide.*—The mixture of α naphthylamine (1·5 g.) and the ester (1.5 g.) was heated in

an oil-bath at 100–105° for three hours. The solid left after triturating with petrol, crystallised from warm, dilute alcohol in colourless needles, m.p. 164°. It gave negative reaction with ferric chloride and concentrated sulphuric acid. (Found : C, 82·2 ; H, 6·0 ; $C_{26}H_{22}ON_2$ requires C, 82·5 ; H, 5·8 per cent.)

1-*β-Naphthylamino-* Δ 1 : 2-*cyclopentene-2-carboxy-β-naphthalide.*—The mixture of the ester (2 g.) and β-naphthylamine (1·8 g.) was heated for three minutes at 180–185° and the cooled mixture was washed with ether. The residue crystallised from warm alcohol in colourless needles, m.p. 184° ; and resembled the α-isomer in chemical properties. (Found : C, 82·5 ; H, 5·8 ; $C_{26}H_{22}ON_2$ requires C, 82·5 ; H, 5·8 per cent.)

Condensation of 4-Methylcyclopentanone-2-carboxylate with Arylamines.

2-*Keto*-1 : 2-*dihydro*-4'-*methylcyclopenteno*-(1' : 2' : 4 : 3)-*quinoline.*—A mixture of 4-methylcyclopentanone 2-carboxylate (3·5 g.) and aniline (2 g.) was heated for four minutes at 145–150°. As attempts to isolate the condensation product in a state of purity failed, the cooled mass was treated with concentrated sulphuric acid (20 c.c.) and warmed for 15 minutes. The solid obtained by pouring the mixture into water crystallised from methyl alcohol in colourless plates, m.p. 249°. (Found : C, 78·4 ; H, 6·7 ; $C_{13}H_{13}ON$ requires C, 78·4 ; H, 6·5 per cent.)

6-*Methyl*-2-*keto*-1 : 2-*dihydro*-4'-*methylcyclopenteno*-(1' : 2' : 4 : 3)-*quinoline* —The mixture of the ester (2·5 g.) and *p*-toluidine (1·3 g.) was heated at 180 for two minutes. As no pure solid could be obtained, concentrated sulphuric acid (15 c.c.) was added to the cooled mixture, and warmed on a water-bath for 20 minutes. The solid obtained by pouring the mixture on ice was washed and crystallised from alcohol when needles, m.p. 230–231° were obtained. (Found : C, 78·5 ; H, 6·7 ; $C_{14}H_{15}ON$ requires C, 78·8 ; H, 7·0 per cent.)

4-*Methylcyclopentanone-2-carboxy*-(1 : 3 : 4)-*xylidide.*—A mixture of (1 : 3 : 4)-xylidine (2·5 g.) and the ester (3 g.) was heated at 180° for three minutes. The mixture gave, on rubbing with petrol (b.p. 40–60°), a solid which was removed and washed with the same solvent. A part of the solid dissolved in cold methyl alcohol, and the solution, on concentration, gave white, silky needles, m.p. 114°. Its alcoholic solution gave dark-green colour with ferric chloride. (Found : C, 73·8 ; H, 7·8 ; $C_{15}H_{19}O_2N$ requires C, 73·5 ; H, 7·8 per cent.)

1-*Xylidylamino-* Δ 1 : 2-4-*methylcyclopentene-2-carboxy* (1 : 3 : 4)-*xylidide.* —The solid insoluble in cold alcohol was soluble in the same solvent on warming, and crystallised in colourless needles, m.p. 180°. It gave negative

tests with ferric chloride and concentrated sulphuric acid. (Found : C, 79·4 ; H, 8·0 ; $C_{23}H_{25}ON_2$ requires C, 79·3 ; H, 8·0 per cent.)

6 : 7-*Dimethyl*-2-*keto*-1 : 2-*dihydro*-4'-*methylcyclopenteno*-(1' : 2' : 4 : 3)-*quinoline.*—A solution of 4-methylcyclopentanone-2-carboxy-(1 : 3 : 4)-xylidide (0·5 g.) in concentrated sulphuric acid (10 c.c.) was heated on a water-bath for 15 minutes, and poured into water, after cooling. The solid crystallised from methyl alcohol in colourless plates, m.p. 215°C. (Found : C, 79·1 ; H, 7·5 ; $C_{15}H_{17}ON$ requires C, 79·3 ; H, 7·5 per cent.)

1-p-*Chloramino*-Δ 1 : 2-4-*methylcyclopentene*-2-*carboxy*-p-*chloranilide.*—A mixture of the ester (2·5 g.) and *p*-chloraniline (2 g.) was heated at 170° for four minutes. After triturating the viscous mass with petrol, the solid was crystallised from alcohol when colourless needles, m.p. 167–168°, were obtained. (Found : Cl, 19·4 ; $C_{19}H_{18}ON_2Cl_2$ requires Cl, 19·7 per cent.) It gave negative tests with ferric chloride solution and concentrated sulphuric acid.

1-p-*Bromanilino*-Δ 1 : 2-4-*methylcyclopentene*-2-*carboxy*-p-*bromanilide.*—A mixture of the ester (2.5 g.) and *p*-bromaniline (2·5 g.) was heated at 180–185° for 5 minutes. The reaction was vigorous and the cooled mass was triturated with petrol. The solid crystallised from alcohol in colourless needles, m.p. 185°, and gave negative tests with ferric chloride and concentrated sulphuric acid. (Found : Br, 35·5 ; $C_{19}H_{18}ON_2Br_2$ requires Br, 35·6 per cent.)

Condensation of the esters with arylamine at higher temperatures.—A mixture of the ester (2 g.) and aniline (2 g.) was rapidly heated to its boiling point in a hard-glass boiling tube and maintained at this temperature for 5 minutes. The reaction was vigorous, and the mixture became viscous on cooling. On rubbing with dilute alcohol, there resulted a solid which, on recrystallisation, gave prismatic needles, m.p. 235° and was identified as Sym-diphenylurea by mixed melting point with an authentic specimen. Other arylamines behaved similarly with this ester as well as its homologue.

We have great pleasure in tendering our thanks to Dr. R. F. Hunter for his kind interest in this work.

Summary of Part II.

The action of various aromatic amines on cyclopentanone-2-carboxylate and 4-methylcyclopentanone-2-carboxylate has been studied, and it has been observed that it is possible to prepare the arylamides and arylimino-amides. The former can be cyclised to carbostyril derivatives.

REFERENCES.

1. Conrad and Limpach, *Ber.*, 1887, **20**, 944 ; 1891, **21**, 523, 1649, 1888 ; 1891, **24**, 2990.
Limpach, *ibid.*, 1931, **64**, 699.
Knorr, *Ber.*, 1883, **16**, 2593; 1884, **17**, 540; 1887, **20**, 1397.
Annalen, 1886, **236**, 69 ; 1888, **245**, 387.
Knorr and Reuter, *Ber.*, 1894, **27**, 1169.
Besthorn and Garben, *ibid.*, 1900, **33**, 3439.
Pellizzari, *Gazetta*, 1891, **21**, 340.
Ewins and King, *J.*, 1913, **103**, 104.
Hurst and Thorpe, *ibid.*, 1915, **107**, 937.
Thielepape, *Ber.*, 1922, **55**, 131.
Gibson, Hariharan, Menon and Simonsen, *J.*, 1926, 2247.
Jadhav, *Journ. Ind. Chem. Soc.*, 1930, **7**, 669 ; 1931, **8**, 681 ; 1932, **9**, 391.
Thomson and Wilson, *J.*, 1933, 1262 ; 1935, III.
Coffey, Thomson and Wilson, *ibid.*, 1936, 856.
2. Dieckmann, *Annalen*, 1901, **317**, 91.
3. Blount, Perkin and Plant, *J.*, 1929, 1977.
4. Kötz and Merkel, *J. Pr. Chem.*, 1909, **79**, 102.
5. Sen and Basu, *Journ. Ind. Chem. Soc.*, 1929, **6**, 309 ; 1930, 7, 435.

DISPERSION OF DEPOLARISATION OF LIGHT-SCATTERING IN COLLOIDS.

Part V. Colloidal Dye-Stuffs.

By R. S. Krishnan.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received May 7, 1937.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

Many dye-stuffs are salts of more or less basic or acidic properties and possess a colloidal nature. They are often hydrolysed and have colloidal tendencies because of this. However, in cases where hydrolysis plays no important part the colloidal character is often quite pronounced, for instance in the alkali salts of the sulpho-acids. In general, those with high molecular weights tend to go into the colloidal state (W. Biltz, 1910). Perhaps the most convincing evidence of the colloidal nature of dye-stuffs is given by the ultra-microscopic observations of Raehlmann, Michaelis and others.

Although most of the work done on dye-stuffs has been concerned with the practical application in textile industry, it has often been attempted from various sides to investigate and characterise the dye solutions. The results are often contradictory, because, in the first place, dyes are not well defined as chemical individuals and one does not know whether the different workers are really dealing with the same substance. Further, the methods of investigation differ in value.

In spite of the fact that much work has been done on ultra-microscopy, diffusion, dialysis, osmotic pressure, conductivity, etc., very little work has been done on the optical properties of colloidal dye-stuffs, especially the study of the absorption of light and Tyndall scattering. The absorption coefficient of a large number of colloidal dye-stuffs were measured by Pihlblad (1918) in the spectral region $\lambda = 2500$–7000 A.U. The dispersed phase of the investigated systems consisted of aniline blue, indophenol, azobenzene, bordeaux, fast red and butter yellow. He studied the light absorption in relation to the degree of dispersion of the particles. No fundamental difference was noticed in the form of the absorption curve when the degree of dispersion was altered except a lateral shift of the absorption maximum in some of the colloids. It was also found that as the size of the colloidal particles increased the absorption curve became flatter and flatter, in accordance with Mie's theory. Very recently, Kortüm (1936) has studied the absorption of light by aqueous solutions of some organic dye-stuffs in

relation to the dispersivity of the ions. Measurements of the validity range of the Beer law in aqueous solutions of dye-stuffs have revealed relationships between the degree of dispersivity on the one hand and ionic magnitude, the number and distribution of hydrophillic groups and stearic influences on the other. Although the study of the absorption of light in colloidal dye-stuffs has been useful to some extent for the determination of the state of dispersivity of ions in solutions, more accurate methods based on the study of the Tyndall effect are particularly suitable for establishing the commencement of micelle formation and therewith the transition from ionic dispersion to colloid-like solutions. The recent investigations of the author (1937) on the dispersion of depolarisation in a large number of colloidal elements have advanced notably our knowledge of the structure of colloidal particles. It is, however, felt desirable to extend these investigations to the case of colloidal dye-stuffs also. In the present paper the results obtained from a study of the absorption and the scattering of light in aqueous solutions of some ten dye-stuffs are given. This investigation should be taken as only preliminary since no attempt has been made to vary the state of dispersion of the dye-stuff ions by the addition of suitable electrolytes. The study of the optical properties of colloidal dye-stuffs which can be obtained in suspension with the particles graded down from those of microscopic to those of molecular dimensions is of great importance to understand the connection between the degree of dispersivity and the kinetics of the dyeing processes.

2. *Preparation of the Sols.*

In the present investigation some ten typical dye-stuffs have been selected for study. The list comprises of colloidal dye-stuff solutions, *i.e.*, those which are completely resolvable under the ultra-microscope, semi-colloids, *i.e.*, those which are partially resolvable and molecular dye solutions, *i.e.*, those which are not resolvable.

Aniline blue.—The hydrosol of this dye-stuff was prepared by adding to 100 c.c. of double distilled water at 90–95°C. 1 c.c. of an alcoholic solution of aniline blue. The concentration of aniline blue in the alcoholic solution was 0·2 g. in 5 c.c. of alcohol.

The other dye-stuff solutions were prepared by dissolving 0·01 g. of the substance in 100 c.c. of water. Since congo rubin is insoluble in water, the sol of this dye was prepared by pouring a solution of the dye in ethyl alcohol into water.

3. *Absorption and Depolarisation Measurements.*

The methods of measuring the extinction coefficients and the depolarisation factors ρ_u, ρ_v and ρ_h from λ 2500–7000 A.U. have already been

described in detail in the earlier parts of this series. The scattering power of the solutions of the dye-stuffs is comparatively weaker than that of the inorganic colloids. Moreover, even in very dilute solutions certain regions of the spectrum are completely absorbed. Consequently the depolarisation measurements could not be pushed through the entire region of the spectrum from 2967–7000 A.U. In such cases the depolarisation curves are discontinuous. In most of these dye-stuffs the depolarisation factors ρ_v and ρ_h were measured only for a single wave-length far away from the region of characteristic absorption. The extinction coefficients for the ten dyes are given in Tables I, III and VI. The values ρ_u, ρ_v and ρ_h after applying the necessary corrections for the finite angle of convergence of the incident beam, are given in Tables II, IV, V, VII and VIII. The curves of absorption and the depolarisation factor ρ_u are reproduced in Figs. 1 to 10.

TABLE I.

Extinction Coefficient.

Wave-length	Aniline blue	Congo red
2250	>1·8	0·7
2500	>1·8	0·55
2750	>1·8	0·3
3000	>1·8	0·4
3250	>1·8	0·63
3500	0·73	0·69
3750	0·43	0·5
4000	0·3	0·39
4500	0·22	0·65
5000	0·5	1·05
5500	0·91	0·6
6000	0·73	0·21
6500	0·47	0·14
7000	0·2	0·09

TABLE II.

Dispersion of Depolarisation ρ_u.

Wave-length	Aniline blue			Congo red		
	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %
3650	4·5	0·28	..	..	..	..
4046	2·5	0·2	11	..	..	..
4358	2	0·15	8·9	..	..	..
4750	2·3	0·5	23	..	..	..
5000	2·9	0·88	49	18	10	100
5500	4·2	1·2	67	20	13	100
6000	3·6	1·05	49	18	11	100
6500	3·3	0·88	..	17	..	..

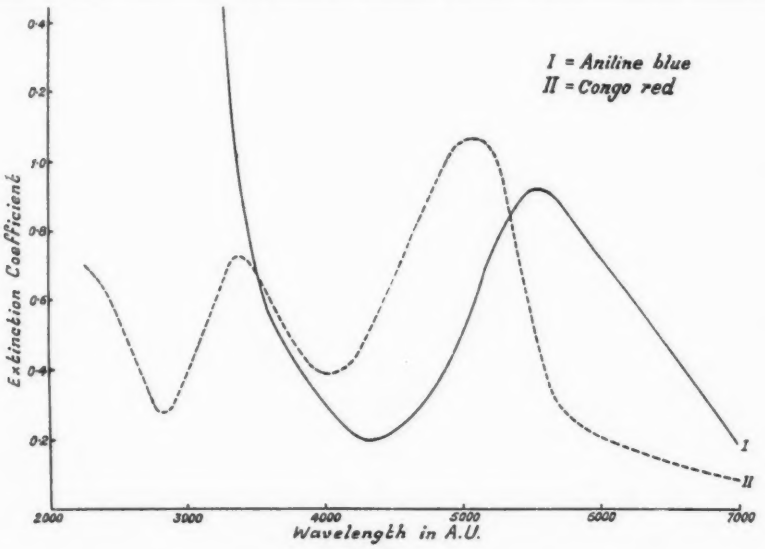


FIG. 1.

Extinction coefficients.

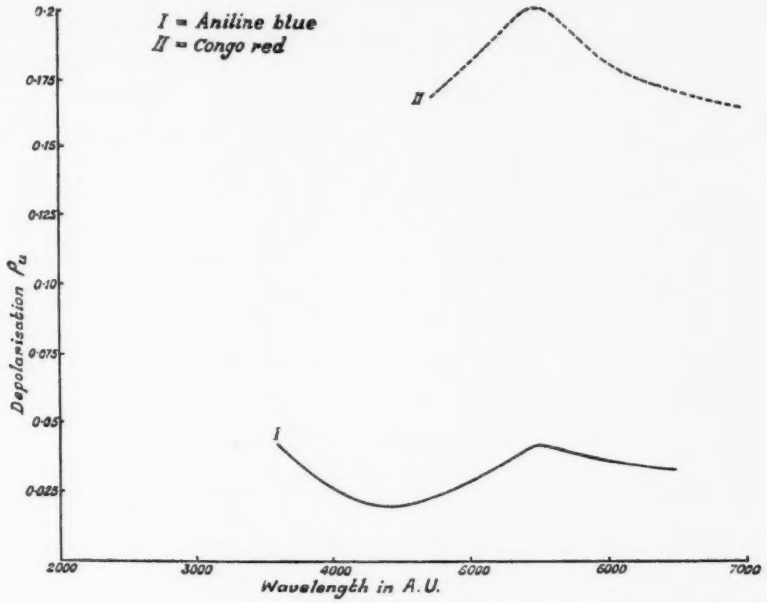


FIG. 2.
Dispersion of depolarisation factor ρ_u.

TABLE III.
Extinction Coefficients.

Wave-length	Iodine green	Nigrosin	Congo rubin	Indigotin
2250	>1·8	1·7	>3	1·2
2500	>1·8	1·7	2·8	1·65
2750	0·95	1·68	1·2	2·45
3000	0·48	1·66	1·36	>3
3250	0·21	1·47	1·86	1·85
3500	0·07	0·78	1·6	1·15
3750	0·02	0·48	1·06	0·38
4000	0·01	0·37	0·96	0·15
4500	0·06	0·54	1·6	0·25
5000	0·18	0·67	>3	0·4
5500	0·44	1·0	>3	1·0
6000	0·85	1·05	0·96	2·75
6500	0·27	0·85	0·27	2·0
7000	0·15	0·7	0·2	0·7

TABLE IV.

Dispersion of Depolarisation ρ_u.

Wave-length	Iodine green			Nigrosin		
	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %
2967	3·0	..	..	46·8	..	..
3650	3·7	..	..	8·4	..	..
4046	5·0	..	..	6·3	..	..
4358	7·0	..	..	7·3	..	..
4750	10·8	4·2	..	14·5	..	..
5000	18·3	5·6	50	19·6	..	..
5500	73	45	65	30·5	..	..
6000	73	65	100	31·8	..	..
6500	28·5	13	..	21·5	..	..
7000	11·7	5·3	..	13·9	4·4	52·7

TABLE V.

Dispersion of Depolarisation ρ_u.

Wave-length	Congo rubin			Indigotin
	ρ_u %	ρ_v %	ρ_h %	ρ_u %
3650	37·5	..	..	6·3
4046	22·8	..	..	5·0
4358	29·8	..	..	4·5
4750	..	..	..	8·0
5000	..	..	..	13·3
5500	30·5	..	..	23·8
6000	14	..	..	34·7
6500	11	..	..	..
7000	8	2·8	55	16·3

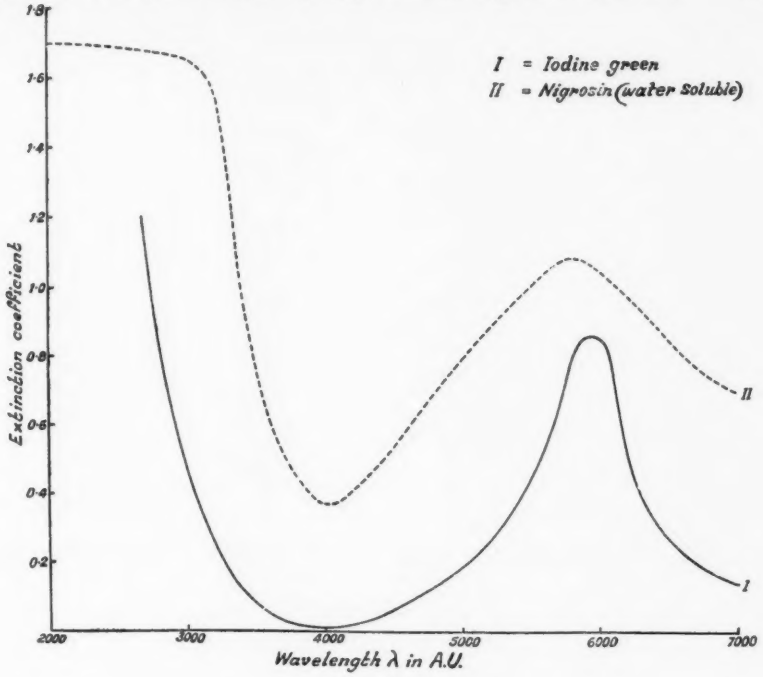


FIG. 3.
Extinction coefficients.

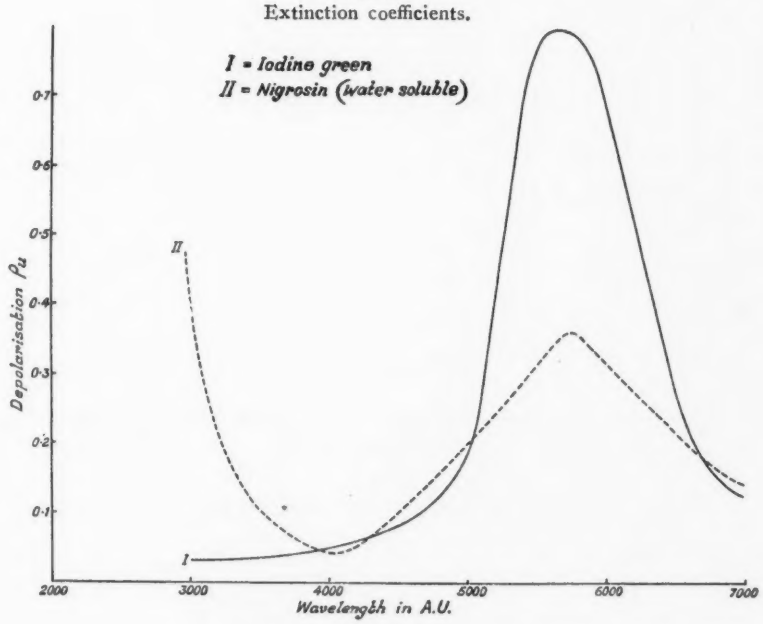


FIG. 4.
Dispersion of depolarisation factor ρ_u.

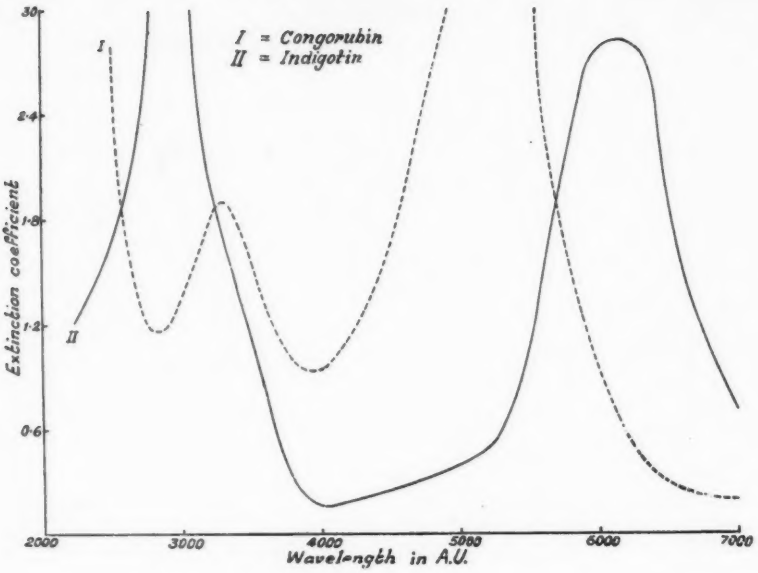


FIG. 5.
Extinction coefficients.

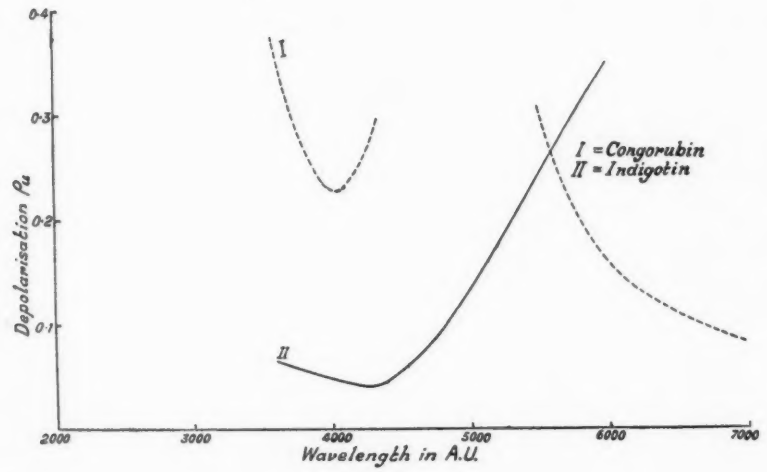


FIG. 6.
Dispersion of depolarisation factor ρ_u.

TABLE VI.

Extinction Coefficients.

Wave-length	Chryosidine	Hoffman's blue	Methyl violet	Orange II
2250	>3	1·8	1·0	>3
2500	1·75	1·5	1·8	>3
2750	1·05	1·0	0·9	>3
3000	0·7	2·6	2·2	2·6
3250	0·45	0·7	0·55	>3
3500	0·4	0·2	0·13	>3
3750	0·9	0·10	0·02	>3
4000	1·8	0·05	0·01	>3
4500	>3	0·6	0·38	>3
5000	>3	3	2·2	>3
5500	0·5	>3	>3	2·4
6000	0·2	>3	>3	0·4
6500	0·075	1·1	3·0	0·32
7000	0·0	0·2	0·25	0·3

TABLE VII.

Dispersion of Depolarisation ρ_u.

Wave-length	Chryosidine			Hoffman's blue
	ρ_u %	ρ_v %	ρ_h %	ρ_u %
2967	..	..	..	8·3
3650	3·1	..	..	5·4
4046	6·9	..	..	5·4
4358	9·5	..	..	7·3
5500	..	..	..	..
6000	25·4	13	100	..
6500	18	8·5	87	11·1
7000	4	1·5	70	7·1

TABLE VIII.

Dispersion of Depolarisation ρ_u.

Wave-length	Methyl violet			Orange II		
	ρ_u %	ρ_v %	ρ_h %	ρ_u %	ρ_v %	ρ_h %
3650	8·4	..	..	..	..	..
4046	12·8	..	..	..	..	..
4358	15·9	..	..	..	..	..
4750	18·6	..	..	..	..	..
5000	23·8	..	..	..	..	..
5500	45·4	..	..	4·0	..	..
6000	82·0	..	..	2·9	..	..
6500	57·6	..	..	2·3	..	..
7000	11·8	3·1	45·5	1·7	0·3	50

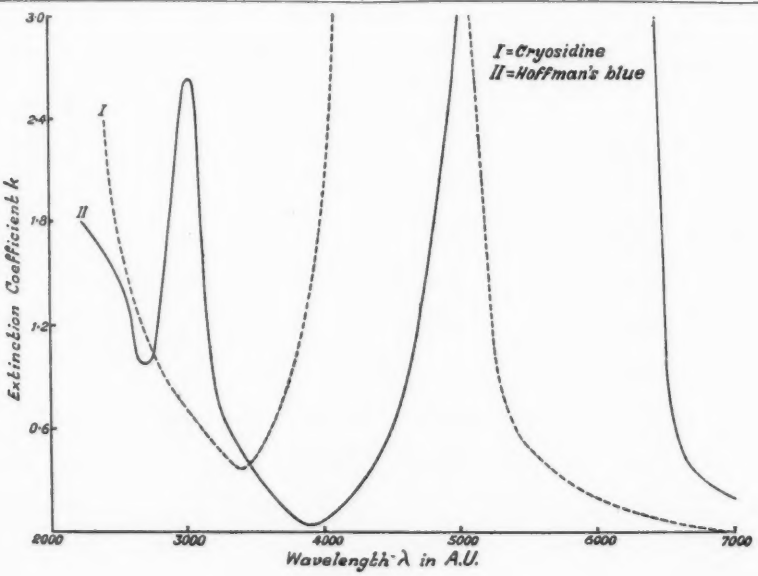


FIG. 7.
Extinction coefficients.

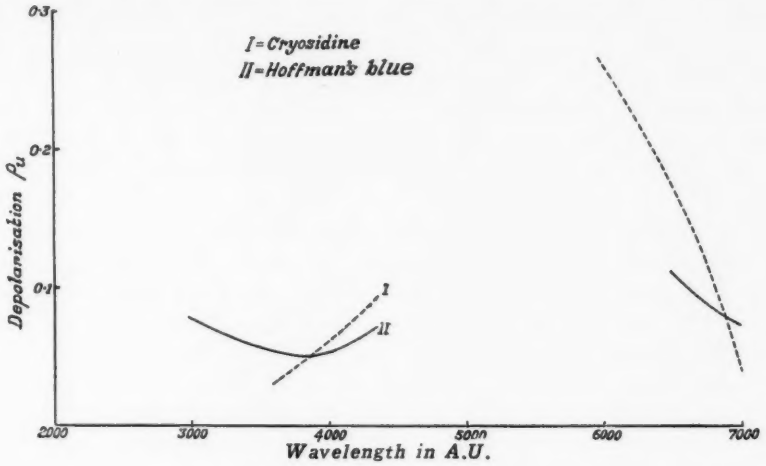


FIG. 8.
Dispersion of depolarisation factor ρ_u.

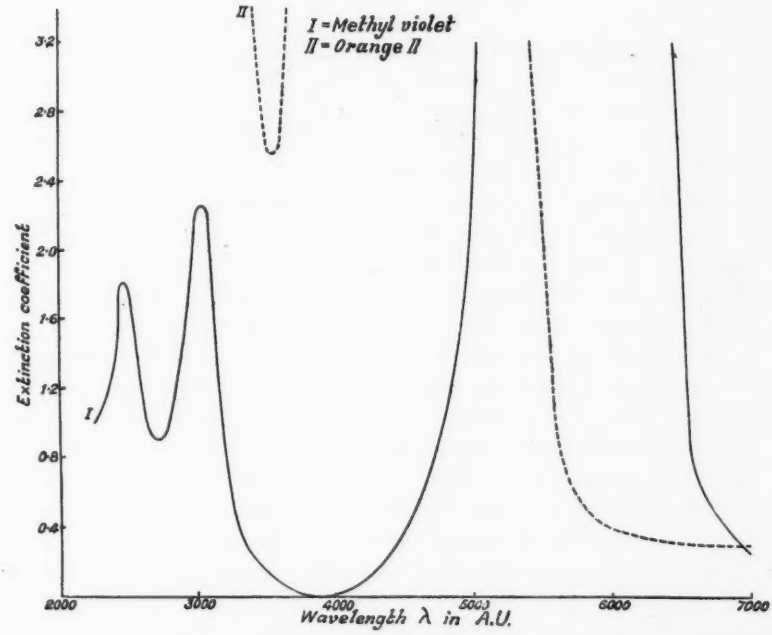


FIG. 9.
Extinction coefficients.

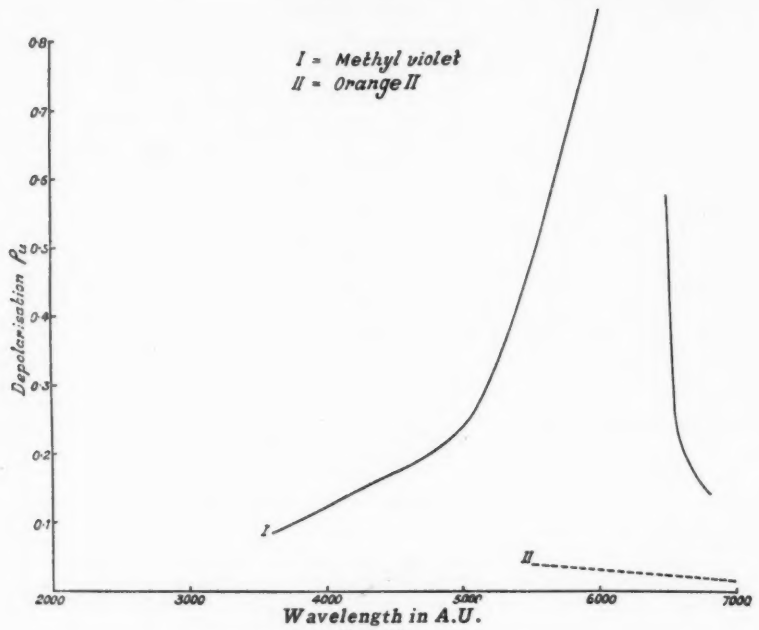


FIG. 10.
Dispersion of depolarisation factor ρ_u.

4. *Discussion.*

A comparative study of the absorption coefficient and the depolarisation factors show that the colloidal organic dye-stuffs behave as do the colloidal metals such as, gold, silver, etc. In the regions of characteristic absorption the depolarisation factors and hence the anisotropy show an enormous increase. In most cases the absorption curves and the depolarisation curves are exactly similar in form. If one side of the maximum in the absorption curve is steeper than the other side, the corresponding side of the maximum of the depolarisation curve is also steeper than the other. Among the ten dye-stuffs investigated, aniline blue, congo red, congo rubin and nigrosin (water-soluble) are typical colloidal electrolytes. Of these aniline blue was obtained very easily in colloidal condition. The scattering power of this sol is considerably greater than that of the other three. The depolarisation measurements show that the solutions of these dye-stuffs contain anisotropic ultra-microscopic micellæ. In congo red solution the anisotropy of the particles is comparatively great, whereas in the case of aniline blue the optical anisotropy is very low.

The solutions of indigotin, Hoffman's blue and iodine green are molecular and not colloidal. The molecules of iodine green are highly anisotropic. In the other two cases because of the low scattering power and intense absorption, the depolarisation factors ρ_v and ρ_h could not be measured accurately with the experimental arrangement employed in the present investigation. The solutions of indigotin and iodine green exhibit a weak fluorescence.

Dyes such as methyl violet, chryosidine and orange II occupy an intermediate position. The solutions of these dyes can be made colloidal by the addition of a suitable electrolyte. In methyl violet solution ρ_u increases enormously as the region of characteristic absorption is reached. The increase is not so much pronounced in chryosidine. Orange II gives the lowest values for ρ_u, ρ_v and ρ_h.

The author's thanks are due to Prof. Sir. C. V. Raman, Kt., F.R.S., N.L., for his kind interest in the work.

5. *Summary.*

The earlier work on the absorption of light by aqueous solutions of organic dye-stuffs has been briefly reviewed. It is pointed out that the study of the optical properties, especially the Tyndall effect, of colloidal dye-stuffs which can be obtained in suspension with the particles graded down from those of microscopic to those of molecular dimensions, is of great importance to understand the connection between the degree of dispersivity and kinetics of the dyeing processes. Measurements of the depolarisation factors ρ_u, ρ_v and ρ_h and the extinction coefficients of aqueous solutions of ten typical dye-stuffs are made for different wave-lengths from 2500 to 7000 A.U. As in the case of metallic sols, such as gold and silver, so also in the case of these dye-stuffs the depolarisation values attain their maximum value in the regions of specific absorption. The depolarisation measurements indicate that the sols of aniline blue, congo red, congo rubin and nigrosin contain anisotropic ultra-microscopic micellæ whereas the solutions of indigotin, Hoffman's blue and iodine green are molecular and not colloidal. The solutions of methyl violet, chryosidine and orange II occupy an intermediate position.

REFERENCES.

Biltz, *Van Bemmelen-Gedenkboek*, 1910, 108.
Kortüm, G., *Zeits. f. Phys. Chem.*, (B), 1936, **34**, 255.
Krishnan, R. S., *Proc. Ind. Acad. Sci.*, (A), 1937, **5**, 94; 305.
Pihlblad, N. E., *Inaugural Dissertation, Uppsala*, 1918.

THE USE OF THE MEDIAN IN TESTS OF SIGNIFICANCE.

By S. R. Savur.

(*Meteorological Office, Poona.*)

Received March 3, 1937.

The arithmetic mean has been in use for such a long time and has consequently and for some other reasons become such a general favourite—even its name has been shortened to " the mean "—that the mere idea of using some other statistical parameter in its place is very likely to be not only looked down upon but also scoffed at by many Statisticians. The general belief is that no other statistic* calculated from a sample has any claim to the seat of honour that has been given to the mean of that sample. We will examine in this paper some of the advantages which the mean is said to possess over similar statistics, and show that those advantages can also be secured by one other at least.

Let us first consider the likely rivals to the mean. They are the mode and the median, if for the present we leave out of consideration the geometric and the harmonic means. We can dismiss the mode at once because it does not possess the essential quality, namely, that a useful statistic should be capable of being determined accurately for a sample. The smaller the sample, the greater is the uncertainty in the determination of its mode. Besides, there may be more than one mode. Thus we are left with the median.

The median can be determined uniquely just as the mean, but far more quickly. This advantage, however, cannot be given much weight. The reasons why the mean has been preferred to the median are the following :—

1. The median is not affected by the *magnitude* of the values so long as a change in the magnitude of any value does not alter its position with regard to the median, whereas the mean depends upon the individual values.

2. The mean is *consistent* and *sufficient* and is the most *efficient* of all statistics.

---

* This beautiful word coined by R. A. Fisher did not find favour in the eyes of Karl Pearson, see the first foot-note on page 49 of (6). Nevertheless it is to be hoped that the word will still continue to be used.

The first reason generally put forward is as the most powerful argument in favour of the mean as against the median, because it is believed that as the mean takes into account the individual values in the sample, it is more representative of the sample and gives more information from the sample than the median. Precisely what this extra information is nobody seems to have taken the trouble to state or even to find out.

Fisher has defined the " amount of information " in a sample and the " amount of information " supplied by any statistic calculated from that sample [(see (12) and (13)], but these definitions have only theoretical interest. Besides, the assumption that is made there is that the distribution of the efficient statistic tends to normality with the increase in the number of individuals in the sample, an assumption which is true in the case of samples drawn from a normally distributed population but may not hold in the case of samples from a non-normally distributed population.

Suppose we are told that the mean of a sample is 30. If on the other hand we are told that the median of the sample is 35, our knowledge about the sample or of the population from which the sample was obtained is neither more nor less than if we had been given only the mean of the sample. By itself, each is as equally useful or useless as the other.

Let us consider the practical use to which the mean of a sample is put. If there is only one sample, we test the significance of its mean. If there be more than one sample we try to find out whether these samples could not have been obtained by mere chance from the same population. These tests are based on the assumption of " normal " (or " not far from normal ") distribution in the populations from which our samples were obtained. We give below better tests than these, better in the sense that they are *independent of the distributions of the individuals in the populations from which our samples were drawn.* Hence the so-called information possessed by the mean of a sample is not of interest, so long as the original distribution is not known.

Let us now turn to the second reason. It is perfectly true that the mean of a sample possesses these characteristics as defined by Fisher, *provided that the sample was drawn from a normally distributed population.* This proviso is the most important and unfortunately it is the greatest stumbling block also. In other cases the mean may lose one or all of these three properties. Fisher, himself, has given on page 321 of (14) an example where he has shown that the mean is an entirely useless statistic for the purpose of determining the mean of that population from a sample drawn from it. Now, it is only in a very few cases such as the tossing of coins, the

throwing of dice, the counting of the number of corpuscles with a hæmacytometer, etc., that we know the form of the frequency-distribution in the population from which our sample has been obtained. *In all other cases we have absolutely no idea of this distribution.* Then what is it that is done in such cases? The most usual procedure has been to assume that our sample was obtained from a population in which the frequency-distribution is either normal or not far from normal. Is this assumption justified? We have to confess that so far no satisfactory justification has been forthcoming. The assumption is made with a feeling (or is it with a hope?) that we may not be far wrong.

Let us consider the full significance of this assumption. We calculate some statistics from our sample, apply certain tests to these statistics and draw appropriate conclusions. The tests are such that these conclusions are quite correct if the frequency-distribution in the population from which our sample was drawn is normal. In other cases they are subject to errors the magnitudes of which depend upon how far the frequency-distribution in the population differs from the normal. Our assumption that this distribution is not far from normal means that we consider that these errors are not material. Hence *the same tests are being applied to samples in all those cases in which the frequency-distributions in the populations from which these samples were drawn are unknown to us.* As we cannot prove or disprove the legitimacy of our assumption, it follows that we can neither show that our deductions are correct, nor find out whether they are wrong. This being the case we do not appear to be better off after applying the tests than if we had not applied them.

We see thus that the tests in use at present may not give, in a number of cases, the information that is sought from them. Further, we are unable to find out which of our deductions, after applying the existing tests, are trustworthy because we are not able to determine definitely which of our samples had been drawn from a normally distributed population. The question then arises, " Are there any tests which are applicable to all cases, that is to say are there tests which are independent of the frequency-distributions in the populations from which our samples are drawn?" The answer is *most certainly yes, and an infinite number of such tests can be devised.* We will consider for the present only those tests in which the median is used.

Credit should undoubtedly go to P. R. Crowe for having boldly espoused recently the cause of the median in his paper.[1] His enthusiasm for the median must have caught H. A. Mathews who followed with his paper ([2]). Still more recently Crowe has given another paper ([3]) on the same subject.

In his paper (1) Crowe has given many advantages which the median possesses over the mean in statistical tests. In addition to these the median has another advantage which is the most important from the statistical point of view, *namely, that using the median we can devise tests which are applicable to samples irrespective of the nature of the frequency-distributions in the populations from which the samples were obtained.* A preliminary note on these tests was given in (4). Before describing these tests we will start with two definitions :—

The definition of the median of a population is well known, namely, it is the value such that there are as many individuals below it as there are above it in that population.

We will use the following definition for the median of a sample.†

If the values (say n in number) in the sample be arranged in the ascending order of magnitude thus

$$y_1 \quad y_2 \quad y_3 \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad y_{n-1} \quad y_n,$$

the median of the sample is

(1) y_{m+1} when $n = 2m + 1$, and

(2) $\frac{1}{2}(y_m + y_{m+1})$ when $n = 2m$

The phrase "the median of a population" will occur so often that it appears necessary to have a special symbol for it. All the likely symbols M, m, and μ have already been used to represent some parameter or other. For this reason I suggested in (4) that the Sanskrit letter म (pronounced like "me" in "calmer" but with the vowel sound slightly less prolonged) may be used for this purpose. The letter appears to be quite appropriate not only on account of its sound but also because it is the first letter of the Sanskrit word मध्यम which means middle or central. As for the sample, its median will be represented by म′.

Thus for "the median of the population from which sample A was obtained" we will write "म of sample A", or merely "म of A", whereas by "म′ of sample A" or "म′ of A" we will mean "the median of the sample A".

Limits for म.—We will now derive two limits between which the म of our sample should lie in order that the sample could have been obtained from that population by random chance.

† For other definitions see Whittaker and Robinson's *Calculus of Observations*, p. 197 (1924 edition). The method for determining the median of a sample suggested by Dunham Jackson is interesting in that he must have been imagining that from that method one will obtain the best approximation to the median of the population from which that sample was drawn.

From the definition of the median of a population we see that the chance is $\frac{1}{2}$ of obtaining a value less than म at random from that population. The chance is also $\frac{1}{2}$ of drawing at random from that population a value greater than म.

Suppose our sample contains n values.

The chance that in a random sample of n values there are not more than l values below म is given by

$$P = \frac{1}{2^n}(1 + {}_nC_1 + {}_nC_2 + \ldots\ldots\ldots + {}_nC_l),$$

$$= I_{\frac{1}{2}}(n - l, l + 1) \quad .. \quad .. \quad .. \quad .. \quad (I)$$

where $I_{\frac{1}{2}}(n - l, l + 1)$ is an incomplete β-function ratio written after the manner of K. Pearson.[7]

For a given value of P and n we can solve equation (I) for l. A method of solution is given below.

Let us choose some limit for random chance, say 5%. We put $P = 0{\cdot}05$ in (I) and solve for l. In general, we will get two consecutive integers such that the corresponding values of P from (I) are on either side of $0{\cdot}05$. We use l_1 the smaller of the two integers.

We now arrange our values in the sample in the ascending order of magnitude thus,

$$y_1 \; y_2 \cdots y_{l_1} \cdots y_{n+1-l_1} \cdots y_n.$$

It is clear that when म is equal to or less than y_{l_1} the chance is less than $0{\cdot}05$ of getting in a random sample of n values not more than l_1 values which are below म ; that is to say, on our 5% limit for random chance our sample could not have been obtained from a population in which म is equal to or less than y_{l_1}. Hence $\text{म} > y_{l_1}$.

Similarly we can see that on the same 5% limit for random chance $\text{म} < y_{n+1-l_1}$. Thus

$$y_{l_1} < \text{म} < y_{n+1-l_1} \qquad \text{(i)}$$

Suppose $y_{l_1} < y_{l_1+1}$ and $y_{n-l_1} < y_{n+1-l_1}$. Now the y's are measured correct to a certain number of significant digits. We increase y_{l_1} and decrease y_{n+1-l_1} by unity in the last significant digit. Let the new values so obtained be denoted by y'_{l_1} and y'_{n+1-l_1}. Then our inequality (i) can be written as

$$y'_{l_1} < \text{म} < y'_{n+1-l_1} \qquad \text{(ii)}$$

Since the limits y'_{l_1} and y'_{n+1-l_1} were determined on the 5% limit for random chance, we will term them the 5% limits for म and the interval y'_{l_1} to y'_{n+1-l_1} (including the limits) the 5% interval for म.

In deriving (ii) we assumed that $y_{l1} < y_{1+1}$ and $y_{n-l_1} < y_{n+1-l_1}$. If, however, $y_{l_1} = y_{l_1+1}$ then $y'_{l_1} = y_{l_1}$, and when $y_{n-l_1} = y_{n+1-l_1}$ we take $y'_{n+1-l_1} = y_{n+1-l_1}$.

In a similar manner we can find the limits and the interval for म on any assumed limit for random chance.

It may be noted in passing that the problem considered here is to some extent the converse of that discussed in ([5]) and ([11]), where equations similar to (I) have occurred. In the problems considered in those papers l (or α in the notation used there) was assumed to be known but the population chance of success was unknown and so the limits to the population chance of success were obtained. In the problem solved here, the population chance of success is known—it is equal to 0·5—while l is not known. Hence the value of l is found from equations like (I).

The म *test of significance.*—We will now give a test of significance which may be stated in the two following forms, the first being applicable to a single sample, while the second when there are two or more samples.

1. The median of a sample is significant (*i.e.*, it is significantly different from zero) on any given limit for random chance, if the interval for म calculated from that sample on that limit for random chance does not contain zero. If zero be an end of that interval, the median can be considered to be just significant.

2. The medians of two samples are significantly different from each other if the intervals (on our limit for random chance) for the corresponding म's do not have a common part. If the higher end of one of the intervals be the same as the lower end of the other, the corresponding म's can be considered to be just significantly different from each other.

Before applying these tests to a few numerical examples we will show how to solve equation (I) for l. There are two methods :—

(*a*) In this, the first method, the tables[7] are used. There is, however, a certain upper limit to n, depending upon the value for P (our limit for random chance), beyond which the tables cannot be used. For such cases the method (*b*) is available. For example, when P = 0·05, n should not be greater than 84, and when P = 0·01, n must not exceed 79 if tables[7] are to be used. The following is the method.

We start with an integral value, say m, slightly less than $\frac{1}{2}n$ and from tables[7] we find $I_{\frac{1}{2}}(n+1-m, m)$. If this be greater than P, our limit for random chance, we find $I_{\frac{1}{2}}(n+2-m, m-1)$, that is, we increase p and decrease q (both in Pearson's notation) by unity. In this manner we will find in general two values $I_{\frac{1}{2}}(n+1-m_1, m_1)$ and $I_{\frac{1}{2}}(n-m_1,$

$m_1 + 1$) such that $I_{\frac{1}{2}}(n + 1 - m_1, m_1) < P < I_{\frac{1}{2}}(n - m_1, m_1 + 1)$. We take $l_1 = m_1 - 1$, that is to say we take the samller value, m_1, of q in these two I-functions and diminish it by unity to get our value for l_1.

(*b*) This method, which is approximate, is applicable for all values of n. The error introduced by this method diminishes very quickly with the increase in n. Although the error may be small, our method of selecting l_1 may occasionally magnify the error into $\pm$ 1 in the calculated value of l_1. When n is large, l_1 is also large, and as will be seen later on an error of ± 1 in l_1 in this case will not affect our results materially.

This method depends upon the fact that the binomial distribution $(\frac{1}{2} + \frac{1}{2})^n$ approaches the corresponding normal distribution very rapidly with the increase in n. The following is the method:

From Table II of ([8]) we find the value of x for which the value of $\frac{1}{2}(1 + \alpha)$ is $1 - P$, P being our assumed limit for random chance. Let the value of x be x_1. Then

l_1 is the integral part of $\frac{1}{2}(n - 1 - x_1\sqrt{n})$ (iii)

The limits for random chance usually adopted are 5% and 1%.

When 5% is the limit for random chance,

l_1 is the integral part of $\frac{1}{2}(n - 1 - 1 \cdot 6449\sqrt{n})$ (iv)

and when 1% is the limit for random chance,

l_1 is the integral part of $\frac{1}{2}(n - 1 - 2 \cdot 3263\sqrt{n})$ (v)

When we use 5% as our limit for random chance, it is a very happy accident that for $n > 84$, in which case tables[7] can be used, there is no error in l_1 as calculated by the relation (iv). *Hence tables[7] are not necessary.* When, however, we use 1% as our limit for random chance, errors in l_1 as calculated from (v) are found only in the following cases for $n > 79$, for all of which tables[7] can be used.

TABLE A.

n	l_1	
	from relation (v)	correct
19	3	4
27	6	7
41	12	13
53	17	18

With this Table A before us we can dispense with the tables[7] *when we adopt* 1% *as our limit for random chance.* Thus, we can completely do away with tables[7] when we use either 5% or 1% as our limit for random chance.

For higher values of n, errors will be introduced occasionally in the values of l_1 calculated by (iv) or (v), but, as mentioned above, the errors will only be $\pm$ 1 and an allowance can always be made for this as shown in example 3 below.

Example 1. To show that the method (*b*) does not introduce a large error even for small values of n we shall apply both (*a*) and (*b*) to the case where $n = 15$. Suppose we take $P = 0 \cdot 05$.

We will use the method (*a*) first. Proceeding in the manner described above we find that $I_{\frac{1}{2}}(11, 5) = \cdot 0592$ and $I_{\frac{1}{2}}(12, 4) = \cdot 0176$. The smaller value of q is 4. Hence $l_1 = 3$.

Let us now use the method (*b*). From (iv) we see that l_1 is the integral part of $\frac{1}{2}(14 - 1 \cdot 645 \times 3 \cdot 872)$ which is $3 \cdot 82$.

Thus $l_1 = 3$, the same result as that obtained by method (*a*).

We will now apply the $\mathfrak{M}$ test of significance defined above to some numerical examples.

Example 2. Let us take the example given on page 113 of Fisher's book.[9] This example relates to the test conducted to find out which of two narcotic drugs (*Dextro-*) and (*Lævo-*)‡ is the more potent. The results are reproduced below :—

TABLE I.

Additional hours of sleep gained by the use of hyoscyamine hydrobromide.

Patient	1 (*Dextro-*)	2 (*Lævo-*)	Difference (2 − 1)
1	+ 0·7	+ 1·9	+ 1·2
2	− 1·6	+ 0·8	+ 2·4
3	− 0·2	+ 1·1	+ 1·3
4	− 1·2	+ 0·1	+ 1·3
5	− 0·1	− 0·1	0·0
6	+ 3·4	+ 4·4	+ 1·0
7	+ 3·7	+ 5·5	+ 1·8
8	+ 0·8	+ 1·6	+ 0·8
9	0·0	+ 4·6	+ 4·6
10	+ 2·0	+ 3·4	+ 1·4

‡ These are abbreviations for *Dextro*-hyoscyamine hydrobromide and *Lævo*-hyoscyamine hydrobromide.

(*a*) Suppose each of the patients had been given the two drugs in succession but in a random order. The last column gives the excess in the hours of sleep produced by (*Lævo-*) over those produced by (*Dextro-*). If the two drugs were equally powerful it is easy to see that the population of these differences in the two durations of sleep is symmetrically distributed about zero. Hence, the median as well as the mean of this population is zero. Our test of significance is thus to see whether median of the sample, in the last column of the table, is significantly different from zero.

To apply the test we arrange the values in the ascending order of magnitude thus

$0{\cdot}0, +0{\cdot}8, +1{\cdot}0, +1{\cdot}2, +1{\cdot}3, +1{\cdot}3, +1{\cdot}4, +1{\cdot}8, +2{\cdot}4, +4{\cdot}6.$

The median, $\mathfrak{M}'$ is $+1{\cdot}3$.

Since $n = 10$, we find that $l = 1$ on the 5% limit for random chance.

Hence y_{l_1} and y_{n+1-l_1} are $0{\cdot}0$ and $+4{\cdot}6$, and y'_{l_1} and y'_{n+1-l_1} are $+0{\cdot}1$ and $+4{\cdot}5$, as $y_2 > y_1$ and $y_{10} > y_9$. Thus the 5% interval is from $+0{\cdot}1$ to $+4{\cdot}5$ (limits included).

This interval does not contain zero, and so we conclude that the *median* of the sample is significantly different from zero, that is to say (*Lævo-*) is significantly more potent than (*Dextro-*).

Fisher using " Student's " *t* test finds that the *mean* of the sample is significantly different from zero.

(*b*) Suppose now that the drugs had been given to twenty different people. In this case we must use the columns under 1 (*Dextro-*) and 2 (*Lævo-*) separately. Arranging the values in the ascending order of magnitude, the values in the two samples are :

(*a'*) $-1{\cdot}6, -1{\cdot}2, -0{\cdot}2, -0{\cdot}1, 0{\cdot}0, +0{\cdot}7, +0{\cdot}8, +2{\cdot}0, +3{\cdot}4, +3{\cdot}7$ and

(*b'*) $-0{\cdot}1, +0{\cdot}1, +0{\cdot}8, +1{\cdot}1, +1{\cdot}6, +1{\cdot}9, +3{\cdot}4, +4{\cdot}4, +4{\cdot}6, +5{\cdot}6.$

The 5% interval for (*a'*) is $-1{\cdot}5$ to $+3{\cdot}6$ and that for (*b'*) is $0{\cdot}0$ to $+5{\cdot}5$. These two intervals have a common part and so the *medians* of the two samples are not significantly different from each other on the 5% limit for random chance. On the *t* test Fisher finds that the *means* of the two samples are not significantly different from each other on the same limit for random chance.

We will now show how to apply the $\mathfrak{M}$ test to those cases in which *n* is quite large. We will take the example 18 on page 110 of (9).

Example 3. A test was conducted to see whether the mean difference in height between the two sexes is significant. The following table, which

is a reproduction of Table 26 on page 110 of(9) with an extra row, gives the distribution of the excess in stature of a brother over his sister in 1401 pairs.

TABLE II.

a	-5	-4	-3	-2	-1	0	1	2	3	4	5	6
b	$\frac{1}{4}$	$1\frac{1}{2}$	$1\frac{1}{4}$	$4\frac{1}{2}$	$11\frac{1}{4}$	$27\frac{1}{2}$	$71\frac{3}{4}$	$122\frac{3}{4}$	$171\frac{3}{4}$	$209\frac{3}{4}$	$220\frac{1}{2}$	$205\frac{1}{2}$
c	$\frac{1}{4}$	$1\frac{3}{4}$	3	$7\frac{1}{2}$	$18\frac{3}{4}$	$46\frac{1}{4}$	118	$240\frac{3}{4}$	$412\frac{1}{2}$	$622\frac{1}{4}$	$842\frac{3}{4}$	$1048\frac{1}{4}$

a	7	8	9	10	11	12	13	14	15	16
b	$148\frac{3}{4}$	$95\frac{1}{4}$	57	26	$11\frac{1}{4}$	$8\frac{1}{2}$	$2\frac{3}{4}$	1	1	$\frac{3}{4}$
c	1197	$1292\frac{3}{4}$	$1349\frac{3}{4}$	$1375\frac{3}{4}$	1387	$1395\frac{1}{2}$	$1398\frac{1}{4}$	$1399\frac{1}{4}$	$1400\frac{1}{4}$	1401

a = Stature difference (in inches); b = Frequency; c = Total frequency from the negative end.

(In the following detailed working of the problem brevity has been purposely sacrificed for clarity in many places.)

There are 1401 values in our sample. Hence the median is the 701th value when the values are arranged in the order of magnitude, that is to say it is some value between 4 and 5 inches (see row c). The variable, the difference in stature, obviously varies continuously and so we can very reasonably assume that the portion of the frequency curve between 4 and 5 is straight as the interval is small. Now, half the frequency listed under 4 is below 4 inches and half that listed under 5 is above 5 inches. Thus there are $517\frac{3}{8}$ ($= 412\frac{1}{2} + \frac{1}{2} \times 209\frac{3}{4}$) values below 4 inches, and $215\frac{1}{8}$ $[= \frac{1}{2}(209\frac{3}{4} + 220\frac{1}{2})]$ values in the interval 4 to 5 inches. Assuming that the frequency curve in the interval 4 to 5 inches is straight, we get

$$\text{the 701th value} = 4 + \frac{701 - 517\frac{3}{8}}{215\frac{1}{8}} = 4 \cdot 8537 \text{ inches.}$$

It is very difficult to measure the height of a person correct to 0·1 inch. Hence it will be more than sufficient if we calculate the median value correct to 0·01 inch at the utmost.

Thus the median of our sample is 4·85 inches.

To find the 5% interval we use (iv). We see that l_1 is the integral part of $\frac{1}{2}(1400 - 1 \cdot 645\sqrt{1401}) = 669 \cdot 2$.

Thus $l_1 = 669$.

The lower limit is the 669th value from the negative end and is 4·71 inches (more accurate value is 4·7095 inches). The upper limit is the 669th value from the positive end and is 5·00 inches (more accurate value is 4·9979 inches), *i.e.*, $y_{669} = 4 \cdot 71''$ and $y_{733} = 5 \cdot 00''$.

To find our y's we must calculate the value of y_{670} and y_{732}. Now the change in height per individual is $1/215\frac{1}{8} = \cdot0046$. Hence $y_{670} = 4\cdot71$ and $y_{732} = 4\cdot99$. We see that $y_{669} = y_{670}$ and $y_{732} < y_{733}$.
Thus the 5% interval is 4·71 to 4·99 (limits included).

This interval does not contain zero. Hence the median of this sample is significant, its म being given by

$$4''\cdot71 \leqslant \text{म} \leqslant 4''\cdot99.$$

Fisher's values, on the assumption of the normal law, are :—

Mean of the sample $= 4''\cdot895$, and the mean of the population is some value between $4''\cdot75$ and $5''\cdot00$.

While explaining the method (*b*) for calculating l_1 it was said that the error introduced in the calculated value of l_1 is occasionally ± 1, and that when l_1 is large this error will not appreciably affect our results. In this example l_1 is the integral part of 669·2 and so we took $l_1 = 669$. If at all this value is in error by 1, its correct value is 668. Assuming this value we get

$$y_{668} = 4\cdot70 \text{ and } y_{734} = 5\cdot00.$$

Since $y_{669} > y_{668}$ and $y_{733} = y_{734}$, we get

$$y'_{668} = 4\cdot71 \text{ and } y'_{734} = 5\cdot00.$$

The 5% interval now comes out as 4·71 to 5·00. Thus *only an insignificant change has been produced in the interval by correcting our value of* l_1 *for a supposed error in it.*

We will take one more example in which Fisher has applied the t test as well as another which he has called a "General" test. This example is given in Fisher's later book.[10]

Example 4. A test was made to see whether cross-fertilised plants grow taller than self-fertilised ones. The data are given in Table 3 on page 41 of ([10]) and are reproduced below in the order of ascending magnitude.

TABLE III.

Differences in eigths of an inch between cross- and self-fertilised plants of the same pair,

$$-67, -48, 6, 8, 14, 16, 23, 24, 28, 29, 41, 49, 56, 60, 75.$$

Let us apply the म test to this sample, namely to see whether the median of the sample is significant.

म′ of the sample is 24.

Since $n = 15$, $l_1 = 3$ [see example (1)] on the 5% limit for random chance.

y_{l_1} and y_{n+1-l_1} are thus 6 and 56.

Hence y'_{l_1} and y'_{n+1-l_1} are 7 and 55 respectively.

म′ is therefore definitely *significant* as the 5% interval 7 to 55 does not contain zero.

Fisher, using the *t* test and the same limit for random chance, finds that the *mean* is *just significant*. He now applies another and more general test, see pages 50–54 of ([10]). On this test he finds that the *mean just fails to be significant*.

To understand this general test consider an infinite population consisting of the differences in length between cross- and self-fertilised plants of the same pair. Let us draw an unlimited number of random samples of 15 values each from this population. We will thus get another infinite population consisting of these samples. In his general test Fisher has confined himself only to a portion of this second population, namely, to those samples in which the individual values are numerically equal to those in our sample. In reality he has restricted himself still further to a part of this portion of the population, for in using only 2^{15} such samples he has virtually assumed that in the original population of these differences the frequency of each of the values (numerically) found in our sample is the same. There is really no justification for this assumption and for this restriction. Hence Fisher's test is not really as general as the म test described in this paper.

In the case of a normal distribution, the mean and the median are the same. Hence when samples are drawn from this population there is bound to be agreement in a large proportion of the cases between the results obtained from the *t* test and the म test. It should, however, be noted that the converse will not necessarily be true, that is to say, if the results of the two kinds of tests agree, we cannot definitely say that the sample has been obtained from a normally distributed population. On the other hand if there is no agreement between the results, we can more definitely conclude that the sample could not have been drawn from a normally distributed population.

Applying these arguments we can conclude that the samples in examples 2 and 3 may have been obtained from a normally distributed population, while that in example 4 could not have been obtained from such a population.

It will be clear from the foregoing that the test suggested in this paper is *independent of the frequency-distribution in the population*, whereas the tests, which are in use at present and in which the mean is used, *depend upon some specific assumption* (*usually the normal law*) *regarding the frequency-distribution in the population*. Hence the test described in this paper is

quite general. This is its greatest merit. In addition another great merit of this test is that its application is far simpler and quicker than that of the t test, especially, when the number of data is large, as in example 3. Hence the suggestion is put forward that the ম test, in which the median is used, may replace the existing ones with advantage.

There is, however, likely to be some opposition in the beginning to this move. This opposition will be mainly due to the *feeling* that as the mean depends upon the individual values in the samples, it must be somehow more representative of the sample than the median. It is intended to discuss this aspect of the matter in more detail in the near future. We will, however, remark in advance that for all practical purposes the so-called advantages of the mean will be found to have but little value and that the median is a far superior statistic for use in significance tests such as those discussed in this paper.

Summary.

In this paper a new test of significance, called the ম test, in which the median is used, is given. It is shown that this test is quite independent of the, to us unknown, frequency-distributions in the populations from which our samples are drawn. The application of this test is quite simple. Hence the test appears to be far better than those in use at present and which are based on some assumed frequency-distribution, generally normal distribution. The ম test is applied to some illustrative examples and the results compared with those obtained after the application of the existing tests.

REFERENCES.

1. P. R. Crowe .. *Scott. Geog. Mag.*, 1933, **49**, 73–91.
2. H. A. Mathews. *Ibid.*, 1936, **52**, 84–97.
3. P. R. Crowe .. *Geog. Review*, 1936, **26**, 463–84.
4. S. R. Savur .. *Curr. Sci.*, 1936–37, **5**, 419–21.
5. ———— .. *Ibid.*, 1936–37, **5**, 385–86.
6. K. Pearson .. *Biom.*, 1936, **28**, Parts I and II.
7. ———— .. *Tables of the Incomplete β-Function*, "Biometrika" Office, Univ. College, London.
8. ———— .. *Tables for Statisticians and Biometricians*, Part I, Camb. Univ. Press.
9. R. A. Fisher .. *Statistical Methods for Research Workers*, 4th edition, 1932.
10. ———— .. *The Design of Experiments*, 1935, Oliver and Boyd, London.
11. S. R. Savur .. *Proc. Ind. Acad. Sci.*, **A**, 1937, **5**, 222–34.
12. R. A. Fisher .. *Proc. Camb. Phil. Soc.*, 1925, **22**, 700–25.
13. ———— .. *Proc. Roy. Soc.*, **A**, 1934, **144**, 285–307.
14. ———— .. *Phil. Trans.*, **A**, 1922, **222**, 309–68.

CRITICAL OPALESCENCE OF LIQUID MIXTURES.

By R. S. Krishnan.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received May 7, 1937.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

The well-known formula of Smoluchowski-Einstein which gives Rayleigh's constant for the polarised coherent scattering due to density fluctuations in any medium, shows that the intensity of this scattering is proportional to the coefficient of isothermal compressibility β. If one approaches the critical point, the coefficient β increases rapidly and consequently one observes an abnormal increase in the intensity of scattering. This phenomenon is called the *critical opalescence*. It is a remarkable phenomenon easily observed but not so easy to interpret. For mixtures of certain pairs of liquids there exists a critical temperature of complete miscibility in the neighbourhood of which one finds a strong opalescence due uniquely to the fluctuations of concentration. The critical opalescence of binary liquid mixtures presents the same optical characteristics as those of pure liquids. The theory of Smoluchowski-Einstein shows that one gets an expression for the intensity of scattering in a liquid mixture by replacing in the expression for the intensity of scattering for a single liquid the coefficient β by a coefficient characteristic of the fluctuations in concentration which becomes infinite at the critical point of complete miscibility. By using carefully purified liquids freed from dust by repeated distillations *in vacuo*, the opalescence in mixtures could be studied over any desired range of temperature and not merely in the immediate neighbourhood of the critical point and very remarkable and interesting changes in the intensity of the scattered light and the state of polarisation are observed. There are certain features of the phenomenon, however, that do not find an explanation on the basis of the Smoluchowski-Einstein theory, one of which is that the depolarisation of the opalescent light remains finite instead of tending to zero as the critical solution temperature is reached. The above theory was afterwards modified by Ornstein, Zernike (1914, 1916, 1918, 1926), Placzek (1930) and Rocard (1933) but with very little success.

In a series of papers in these *Proceedings* (Krishnan, 1934–35) the author presented evidence for the first time that large molecular clusters exist in such liquid mixtures in the neighbourhood of the critical solution temperature. The essential idea involved in the author's experiments is the examination of the state of polarisation of the transversely scattered light when a beam of plane polarised light with its electric vector horizontal is passed through the medium. In such a case the scattering in the transverse horizontal directions would be completely unpolarised, *i.e.*, its depolarisation factor would be unity provided the scattering centres are of molecular dimensions. Any departure from the value of unity would therefore indicate that the scattering centres are no longer of molecular size but possess dimensions not small compared with the wave-length of light. The finite value of the depolarisation of the opalescent light arises from this fact.

Almost simultaneously with the author's discovery of molecular clustering in liquid mixtures, Rousset (1934) reported some quantitative data regarding the state of polarisation of the light scattered by binary liquid mixtures in the neighbourhood of the critical solution temperature. He finds that as one approaches the critical temperature, the depolarisation factor ρ_u diminishes at first and after attaining a minimum very near the critical solution temperature increases again rapidly. By assuming that the primary scattering is completely polarised he has attempted to explain the rapid increase of ρ_u in the immediate neighbourhood of the critical point by the existence of a secondary scattering partially depolarised, the intensity of which increases more rapidly than that of the primary scattering, if ΔT is sufficiently small. ΔT is the difference of temperature between any particular temperature and the critical solution temperature. The anomalous depolarisation observed in the neighbourhood of the critical point when the incident light is polarised with vibrations horizontal has been attributed by Rousset to secondary scattering, whereas the present author has attributed it to the presence of molecular clusters. A study of the dispersion of depolarisation of light-scattering in liquid mixtures very near T_c will be a decisive test. The recent investigations of the author (1937) on the dispersion of depolarisation of light-scattering in colloids have clearly shown that if there is any tendency for the formation of molecular clusters of size comparable with the wave-length of light, the depolarisation factors should exhibit an appreciable dispersion with wave-length. Hence it was thought desirable to go into this question in detail in order to decide once for all whether all the anomalies observed at the critical solution temperature of liquid mixtures could be explained on the basis of the formation of

molecular clusters or not. At first a brief resumé of the theory of secondary scattering as propounded by Rousset will be given and also the further consequences of this theory which has not been considered by him. These are tried out experimentally and the results are also given. Measurements of the intensity and the depolarisation factors ρ_u, ρ_v and ρ_h were made for three more binary mixtures and one ternary mixture over a range of temperature of about 30° above the critical solution temperature. A critical study of the theory of Gans (1936) has been made in relation to the experimental results obtained by the author from a detailed study of light-scattering. The bearing of these results on the anomalies of viscosity, magnetic birefringence, flow birefringence, etc., noticed in the vicinity of the critical solution temperature has also been discussed in detail in the present paper.

2. *Theory of Secondary Scattering.*

The principle underlying the calculations of Rousset is that when a beam of linearly polarised light is incident on a small volume of a mixture of two liquids, each individual volume element inside the mixture becomes a luminous source vibrating parallel to the incident electric vector and sends out radiations which he calls as the *primary scattering*. This in turn forms the source of exciting radiation. Each individual volume element under the influence of the primary scattering by all the other elements becomes a doublet and sends out radiations again. This he calls as the *secondary scattering*. Since the intensity of the primary scattering increases as the critical solution temperature is approached, the intensity of the secondary scattering also correspondingly increases and influences the observed depolarisation values.

CASE I. *Incident light and consequently the primary scattering vibrate parallel to OZ.*—

Let X_z and Z_z be the components parallel to OX and OZ respectively of the secondary scattering in the transverse horizontal direction OY. They are given by the following triple integrals,

$$X_z = \iiint_V \sin^3\theta . \cos^2\theta . \cos^2\phi . \, d\theta , \, d\phi . \, dr .$$

$$Z_z = \iiint_V \sin^5\theta . \, d\theta . \, d\phi . \, dr . \qquad .. \qquad (1)$$

where θ, ϕ and r are the spherical co-ordinates of the particular volume element under consideration.

CASE II. *The incident light and the primary scattering are polarised with vibrations parallel to OY.*

The components X_y and Z_y of the secondary scattering are given by

$$X_y = \iiint_V \sin^5\theta.\ \cos^2\phi.\ \sin^2\phi.\ d\theta.\ d\phi.\ dr.$$

$$Z_y = \iiint_V \sin^3\theta\ \cos^2\theta.\ \sin^2\phi,\ d\theta.\ d\phi.\ dr. \qquad (2)$$

The integration should be extended throughout the volume of the mixture on which the light is incident.

If the scattering volume is in the form of a disc of radius R and height 2 H with its axis parallel to the Z-axis, the components of the secondary scattering for the two cases are given by

$$Z_y = X_z = \frac{\pi}{4}\left[R \text{ arc tan } \frac{H}{R} + R^2\, H/(R^2 + H^2)\right]$$

$$X_y = \frac{Z_z}{8} = \frac{\pi}{4}\left[\tfrac{3}{4}\, R \tan^{-1}\frac{H}{R} - \tfrac{1}{4}\,\frac{R^2H}{R^2 + H^2} + H.\log_e \frac{H^2 + R^2}{H^2}\right] \qquad (3)$$

Since the primary scattering is supposed to be completely polarised, one does not observe it along the transverse direction OY when the incident beam is polarised with vibrations parallel to OY. But the two components X_y and Z_y of the secondary scattering which are observed, are not of the same intensity ; the depolarisation ρ_h of the secondary scattering is given by the ratio Z_y/X_y.

$$\rho_h{}^* = \frac{Z_y}{X_y} = \frac{1}{\frac{1}{4} + \log_e \frac{R}{H}}, \qquad (4)$$

when H is small compared with R. For R = 10 H, $\rho_h = 0{\cdot}39$, *i.e.*, less than unity.

From further calculations he has shown that the components Z_y and X_z are not localised on the primary radiation but are of the same intensity throughout the whole volume of the fluid. The components Z_z and X_y have the maximum intensity at the centre of the primary track and the intensity diminishes as one goes farther away from the centre, the rate of diminution being governed by the ratio R/H. The whole result can be summarised schematically as shown in Fig. 1.

---

* Rousset has taken ρ as equal to $\frac{X_y}{Z_y} = \frac{1}{4} + \log_e \frac{R}{H} = 2{\cdot}6$ when $\frac{R}{H} = 10$.

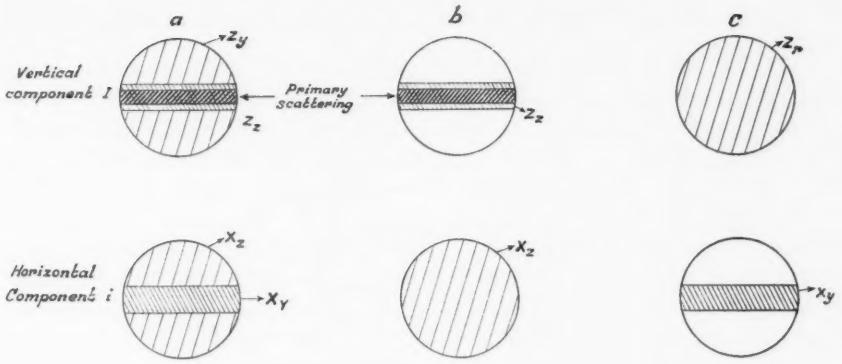


FIG. 1.

CASE 1. *Incident light is unpolarised.*—According to Rousset's calculations the vertical component I of the scattered light consists of a very intense pencil due to the primary scattering which is widened out owing to the superposition of the component Z_z of the secondary scattering and a background illumination due to the existence ot the component Z_y of the secondary scattering (see Fig. 1 *a*). The horizontal component *i* consists of a diffuse track in the centre due to the component X_y and a background due to the component X_z. If one observes the scattered light through a Wollaston prism, one obtains a finite value for the depolarisation factor ρ_u.

CASE 2. *Incident light is polarised with vibrations parallel to OZ.*—The trace of the pencil disappears in the image *i* which reduces itself to a background illumination produced by the component X_z of the secondary scattering. One will find therefore that the factor of depolarisation ρ_v is zero (see Fig. 1 *b*).

CASE 3. *Incident light is polarised with vibrations parallel to OY.*—The trace of the incident beam disappears in the image I which is reduced to a background scattering provided by the component Z_y. In the image *i* there exists the component X_y with its edges more or less diffuse. For this case ρ_h is zero (see Fig. 1 *c*).

In an actual experiment the scattering vloume of the mixture is in the form of a rectangular parallelopiped of sides, 2 *a*, 2 *b* and 2 *c*, 2 *b* and 2 *c* the width and height of the track respectively, being small compared with the length 2 *a*. For such a case the conclusions detailed above are valid. The value of ρ_h depends on the ratio c/a.

3. Critical Remarks on the Theory of Secondary Scattering.

1. Although the intensity of scattering is comparatively greater near the critical solution temperature T_c, it is only a small fraction of the intensity of the incident light. For $\Delta T = 4°C.$, ($\Delta T = T - T_c$), the intensity of scattering in water-isobutyric acid mixture is only 25 times that of pure benzene. (This value is taken from Rousset's measurements.) The Rayleigh's constant for benzene is equal to 10^{-5}. The Rayleigh's constant for the mixture is therefore equal to $2 \cdot 5 \times 10^{-4}$. So the ratio of the intensity of the secondary scattering to that of the primary scattering at $\Delta T = 4°C.$ is equal to $2 \cdot 5 \times 10^{-4}$. Since the primary scattering is completely polarised and the secondary scattering is depolarised to the extent of $\frac{1}{8}$, the value of ρ_u will be of the order of $0 \cdot 003$ per cent. But the actual observed value of ρ_u, after making due allowance to convergence of the incident beam, is 1.5 per cent. Supposing for a moment (as Rousset has remarked), that this $1 \cdot 5$ per cent. arises partly due to the depolarised orientation scattering and partly due to the depolarised secondary scattering, the orientation scattering should be 100 times more intense than the secondary scattering. Consequently at this temperature ρ_h should not be appreciably less than unity. But in all the mixtures investigated the value of ρ_h is unmistakably of the order of 0.2. This low value of ρ_h can, therefore, be only ascribed to the existence of molecular clusters.

2. It is well known that the orientation scattering does not vary appreciably with temperature provided the composition of the mixture is kept constant. The intensity of the secondary scattering is proportional to the intensity of the primary scattering which increases as T_c is approached. According to Rousset, $\rho_h = O/(O + S)$ where O is the component of the orientation scattering and S is the component of the secondary scattering. From a knowledge of the values of ρ_h at various temperatures the relative intensities of the secondary scattering at those temperatures could be evaluated. The rate of increase of the secondary scattering with decrease of ΔT should be at least equal to that of the primary scattering, if not more. From a comparison of Tables I and II, one is led to believe that this is far from being the case. The values of ρ_h and the intensity of scattering for phenol and water are taken from one of the author's earlier papers.

3. According to Rousset's theory, the intensity distribution of the primary opalescent scattering is symmetrical about the direction perpendicular to the direction of the incident beam. But it has been observed by various investigators including Rousset that the scattering in the forward direction is more intense than the scattering in the backward direction.

TABLE I.
Phenol and Water.

Temperature °C.	ρ_h observed %	Relative intensities of secondary scattering (calculated)	Relative intensities of primary scattering (observed)
95	75	1 (assumed)	1 (assumed)
90	66	1·5	1·2
87·5	61	1·91	1·3
83	51	2·9	2·1
80	47	3·4	2·9
77	39	4·69	3·8
74	31	6·7	7·8
69·5	16	15·8	45
69	12	22	53·0

TABLE II.
Phenol and Normal Hexane.

Temperature °C.	ρ_h observed %	Relative intensities of secondary scattering (calculated)	Relative intensities of primary scattering (observed)
74	100	..	1 (assumed)
64	80	1 (assumed)	1·14
59	75·5	1·03	1·33
57	72	1·56	1·66
50	63	2·4	3·1
45	55·8	3·24	5·45
42·9	44	5·48	14
41·2	25	12	30

This Mie effect is characteristic of the scattering by particles whose size is comparable with the wave-length of light.

4. If the opalescent scattering is really molecular in origin it should obey λ^{-4} law. Andant (1924), Rousset and others have found that very near the critical solution point the law of scattering is λ^{-n} where n is definitely less than 4. This fact of observation finds an easy explanation on the basis of *Schwarmbildung*.

5. According to Rousset's theory, when the incident beam is unpolarised or polarised with vibrations horizontal, the horizontal component of the light scattered in the transverse horizontal direction will be comparatively more diffuse, the intensity being maximum at the centre of the track and gradually falling off on either side. The track should also appear broader than the corresponding vertical component. This was tested out experimentally. Figs. 2(*a*) and 2(*b*) in Plate XIX represent the photographs of the light scattered by a mixture of phenol and hexane very near T_c taken through a double-image prism, when the incident light is unpolarised and polarised with vibrations horizontal respectively. Figs. 3(*a*) and 3(*b*) represent the corresponding photographs taken through a double-image prism and a nicol, the nicol being so oriented as to equalise the two mutually perpendicular components. In all the cases the width of the track is the same for the two components. The distribution of intensity is also uniform throughout the cross-section of the tracks.

6. If $2a$ and $2c$ are the length and vertical depth of the track inside the medium, the values of ρ_u, ρ_v and ρ_h are functions of the ratio c/a according to the theory of Rousset. ρ_u and ρ_h should increase or decrease *pari passu* with c/a, whereas the variation of ρ_u should be in the opposite direction.

7. Since the secondary scattering depends only on the intensity of the primary scattering the observed values of the depolarisation factors should not exhibit any appreciable dispersion with wave-length. Table III gives the values of ρ_u, ρ_v and ρ_h measured for a mixture of phenol and normal hexane which was maintained a few degrees above the critical solution temperature, with different colour filters and for two different values of c/a.

The observed dispersion of depolarisation is not due to fluorescence for any trace of fluorescence will try to increase all the three quantities ρ_u, ρ_v and ρ_h and not only two of them. From a comparison of the observed dispersion of depolarisation with that observed in the case of inorganic sols which

TABLE III.

	$c/a = 0{\cdot}33$		$c/a = 0{\cdot}05$	
	Blue filter %	Orange filter %	Blue filter %	Orange filter %
ρ_u	1	0·54	1	0·48
ρ_v	0·21	0·1	0·23	0·09
ρ_h	22·0	24	21	25

do not possess any specific absorption (Krishnan, 1937) it can be inferred that the effect is really due to the finite size of the scattering particles and not due to secondary scattering.

8. According to the theory of Rousset, when the incident light is unpolarised the background scattering at points far away from the track should be completely unpolarised. If the plane of polarisation of the incident beam is horizontal the plane of polarisation of the background scattering will be vertical. If, on the other hand, the plane of polarisation of the incident beam is vertical, the background scattering should be completely polarised with vibrations horizontal. For different states of polarisation of the incident beam, the state of polarisation of the background scattering as seen in the transverse direction has been determined by means of a movable slit kept at points situated along a vertical at different distances from the centre of the track. The measurements were made with a phenol-hexane mixture very near the critical solution temperature and also with a casein solution the p_H of which was adjusted so as to show an intense opalescence. The results are given in Table IV.

It is well known that in casein solution the protein molecules are very large in size. The similarity in the behaviour of the liquid mixture and the casein solution indicates that the scattering elements in the liquid mixture should also be molecular clusters of size comparable with the wave-length of light and not the individual molecules. In this connection the observations made on the nascent precipitate of sulphur formed when a little acid is added to a dilute and well filtered solution of hyposulphite will be of some interest. The light scattered transversely by the sulphur sol was observed through a double-image prism. In the early stages of the formation of the

TABLE IV.

The Width of the Track inside the Medium = 0·2 *cm.*

Medium	Position of the movable slit	ρ_u %	ρ_v %	ρ_h %
Phenol and hexane ..	Slit on track	0·7	0·31	36
	Slit just below track	6	2·8	49
	Slit 2 cm. below track	19·8	13·6	88·5
Casein solution measured with red light	Slit on track	1·73	0·7	42
	Slit just below track	22·7	10·5	95
	Slit 3 cm. below track	75	95	100

sol the double-image prism suitably rotated showed complete polarisation of the light scattered transversely. Somewhat later the minimum light seen transversely showed Tyndall's residual blue, indicating that for this colour the polarisation was no longer complete, while for the red colour it was more complete, the increase in wave-length compensating the growth of the particles. As the particles were allowed to grow, a stage was reached when the effects for blue and red light were well contrasted. A similar observation was made with one of the binary mixtures. The mixture was initially kept at about 25° C. above the critical solution temperature and was allowed to cool. A beam of light was focussed into the mixture and the scattered light was observed through a double-image prism and nicol. The nicol was used so as to equalise the intensity of the two components. As the temperature was slowly lowered the horizontal component was more bluish than the vertical component, the effect being most pronounced at the critical solution temperature.

From what has been said above it can be inferred that in the neighbourhood of the critical solution temperature of liquid mixtures, the molecules have got a tendency to group themselves together in the form of clusters and that the finite value of the depolarisation arises due to the fact that the size of the clusters becomes comparable with the wave-length of light.

4. Experimental Results Obtained with a Few More Liquid Mixtures.

The measurements of the depolarisation factors ρ_u, ρ_v and ρ_h were made for the following mixtures, phenol-normal hexane, phenol-normal heptane, aniline-normal heptane and benzene-acetic acid-water. The photo-electric method was employed for comparison of the intensities of scattering by these mixtures at various temperatures above the critical solution temperature. Very near T_c the depolarisation factors were also measured with coloured filters also. The results are tabulated below. The intensity of scattering was measured using incident white light only. Necessary corrections are applied for the convergence of the incident beam.

The results obtained with the three binary mixtures confirm the author's conclusions regarding the formation of molecular clusters, which are discussed in detail in the earlier papers. The ternary mixture studied, also exhibits the same phenomenon. At the critical solution temperature the composition scattering which is completely polarised becomes large and the scattering due to the finite size also increases. The combined effect gives a finite value for the depolarisation ρ_u. As soon as the critical fog or the emulsion begins to appear a considerable increase in the size of the

TABLE V.

49% *Phenol and* 51% *Normal Hexane.*

Temperature	Colour of the filter used	ρ_u %	ρ_v %	ρ_h %	Relative intensity of scattering
71		1·4	0·62	100	1 (assumed)
62		1·0	0·45	84	1·25
55		0·6	0·25	78	2·75
50		0·49	0·19	59	6·25
47·5		0·43	0·14	42	11·4
46·5	orange	0·35	0·09	42	17·8
46·5	blue	0·65	0·12	24	
44·5	blue	0·55	0·09	12	43·8

TABLE VI.

54.2% *Phenol and* 45.8% *Heptane.*

Temperature	Colour of the filter used	ρ_u %	ρ_v %	ρ_h %	Relative intensity of scattering
74		2·5	1·25	100	1 (assumed)
64		1·8	0·8	80	1·14
59		1·6	0·7	75·5	1·33
57		1·4	0·6	72	1·66
50		1·0	0·27	63	3·1
45		0·54	0·16	55·8	5·45
42·9		0·49	0·12	44	14
42·6	orange	0·36	0·1	55	18
42·6	blue	0·58	0·16	40	
41·2	orange	0·43	0·1	30	30
41·2	blue	0·61	0·12	20	

TABLE VII.

56% *Aniline and* 44% *Normal Heptane.*

Temperature	Colour of the filter used	ρ_u %	ρ_v %	ρ_h %	Relative intensity of scattering
85		2·8	1·4	100	1 (assumed)
74		1·8	0·75	84	1·5
68		1·2	0·46	80	2·7
66		0·92	0·36	65	4·8
63		0·5	0·16	50	5·1
61·5	orange	0·44	0·08	32	8
60·8	orange	0·36	0·06	19	12

TABLE VIII.

Benzene, Acetic Acid and Water Mixture.

Temperature	Colour of the filters used	ρ_u %	ρ_v %	ρ_h %
54		4·1	2·0	100
48		3·1	1·3	93
45		1·7	0·7	81
40		0·9	0·31	70·5
38		0·67	0·22	65·5
37	blue	1·0	0·31	45
37	orange	0·6	0·22	55
37	red	0·4	0·15	
36	blue	0·74	0·12	37
36	orange	0·35	0·1	15

clusters formed takes place resulting in an increase in the value of ρ_u. In the case of the phenol-heptane mixture it was possible to detect the increase in the value of ρ_u even before the critical solution temperature was approached. This is because very near T_c the rate of increase of the depolarised size scattering with diminution of temperature is greater than the rate of increase of polarised composition scattering. This explains why Rousset observed an increase in the value of ρ_u very near T_c in some of the mixture studied by him. The fact that the dispersion of depolarisation is most pronounced at the critical solution temperature shows clearly that the size of the clusters formed is greatest at this temperature.

5. *Theory of Gans.*

Soon after the publication of the results on the molecular clustering in binary liquid mixtures by the author, Gans (1936) put forward a theoretical explanation of the observed anomalous depolarisation (*i.e.*, $\rho_h < 1$), on the basis of the swarm-formation in fluids. He has considered this problem from the standpoint of the theory of fluctuations under the simplifying

assumption that besides the density variations there are accidental variations of isotropy or orientation variations due to the formation of molecular groups, and that the linear dimension d is so small that $d^2 \ll \lambda^2$. Gans has derived a relation between the degree of depolarisation ρ_h and the form of the molecular aggregates. If the groups are spherical in shape ρ_h has its limiting value of unity. If on the other hand the groups are in the form of thin rods of length l,

$$\frac{1}{\rho_h} = 1 - \frac{4\pi^2 l^2}{42 \lambda^2} \tag{5}$$

For discs of radius r,

$$\frac{1}{\rho_h} = 1 + \frac{4\pi^2 r^2}{14 \lambda^2} \tag{6}$$

Katalinic and Vrkljan (1936) have extended Gans' theory. General conditions for the occurrence of the anomalous depolarisation for the case of three dimensional molecular swarms are derived by them without making too exact assumptions as to their form.

According to Gans' theory ρ_h should be greater as well as less than unity depending upon the shape of the swarms. But in all the mixtures studied so far, ρ_h is found to be less than unity and never greater than unity. It is also hard to believe that the clusters are of the same shape in all the mixtures. This is because of the limitations of Gans' theory. The theory is valid only for swarms whose linear dimension is such that $d^2 \ll \lambda^2$. For such small clusters only the first electric partial wave, *i.e.*, the dipole radiation, is usually taken into consideration. For large molecular clusters one has to take into consideration the higher electric partial waves as also the magnetic partial waves as indicated in Mie's theory.

6. *Other Experimental Evidence.*

Various other physical properties such as viscosity, flow birefringence, electric and magnetic birefringence, X-ray diffraction, etc., have been extensively studied by numerous investigators and the results obtained are intimately connected with the conclusions arrived at from light-scattering experiments. Reference to some of these properties has already been made in the author's earlier papers.

A systematic study of the viscosity of binary liquid mixtures at various temperatures and for various concentrations has been carried out by Zofia Szafranska (1935). It is found that when the solutions show no optical anomalies there is no trace of viscosity irregularity, whereas for mixtures which show optical anomalies he finds an abnormal increase in the viscosity

near the critical solution temperature. The increase is most pronounced for mixtures having the exact critical composition. The viscosity of the three component system, benzene-ethyl alcohol-water, has been measured in the neighbourhood of the critical point by Kimura (1936) and similar results have been obtained by him. These anomalies find an easy explanation on the basis of molecular clustering. The sudden increase of viscosity is caused by the existence of molecular aggregates, the increase being very much governed by the size of the aggregates which in turn is a function of the temperature of the mixture and also its composition.

The Kerr-effect in mixtures of nitrobenzene and heptane in the neighbourhood of T_c has been studied recently by Goldet (1936). The observed effect increases rapidly as the critical temperature is approached. The abnormal increase may be attributed to the formation of clusters.

7. *Conclusion.*

Critical composition mixtures near the critical point are usually regarded as colloidal emulsoids. It is well known that a substance will show the characteristics of a colloid if it contains particles graded down from those of microscopic to those of molecular dimensions. If on cooling a mixture a milky emulsion is obtained observation through a microscope will at once indicate that the medium contains particles whose diameters are of the order of the wave-length of light. On the other hand, the critical composition mixture very near the critical solution temperature, is more like a system which is intermediate between the two extreme cases, *i.e.*, the coarse disperse system and the molecular disperse system. The critical solution mixtures do not show any milky turbidity, but they show an opalescence which is characterised by double colour, *i.e.*, yellow by transmitted light and blue by scattered light. Optical investigations with an ordinary microscope do not reveal the existence of discrete particles. We find this type of opalescence in many typical colloidal systems, for example, in many protein solutions in which also no discontinuity can be traced with an ordinary microscope. At the critical point the vapour pressure is independent of concentration. The same phenomenon has been observed by Tammann in gelatin and gum arabic solutions. It may be remarked that the large increase in opalescence as well as the existence of pronounced minima in the values of ρ_u, ρ_v and ρ_h at the critical solution temperature of binary liquid mixtures bear a striking similarity to the observations of Subbaramaiah (1937) at the iso-electric point of protein solutions. But in spite of the similarity in optical behaviour, there are certain important characteristics of protein solutions which are not exhibited by mixtures.

The protein solutions progressively change with time. But it is a fact of observation that critical opalescence and such other phenomena exhibited by critical solution mixtures are invariant with time and depend only on the temperature of the mixture.

In conclusion the author takes this opportunity to express his grateful thanks to Professor Sir C. V. Raman, Kt., F.R.S., N.L., for his kind and helpful interest in the work.

8. *Summary.*

A critical review of the theory of secondary scattering proposed by Rousset in order to explain the finite value of the depolarisation of the opalescence of liquid mixtures is given. Further consequences of the theory of secondary scattering have been worked out and it is found that the experimental results obtained are not in accordance with the conclusions of the theory. From the results obtained it has been concluded that in the neighbourhood of the critical solution temperature of liquid mixtures the molecules have got a tendency to group themselves together in the form of clusters and that the finite value of the depolarisation of the opalescent light arises due to this fact. In the neighbourhood of T_c the secondary scattering has little or no effect on the depolarisation factor, although it may have an appreciable effect for $\Delta T < 0{\cdot}1^\circ$ C. where $\Delta T = T - T_c$. The measurements of the depolarisation factors ρ_u, ρ_v, and ρ_h for three binary mixtures and one ternary mixture have been made over a range of temperature of 30° above T_c. The results obtained fully confirm the author's earlier report regarding the existence of clusters in liquid mixtures not only at the critical solution temperature but also at temperatures considerably removed from it. The theory proposed by Gans has been discussed in relation to the experimental results obtained by the author and the limitations of the theory have also been pointed out. The bearing of the results on the anomalies of viscosity, electric birefringence, etc., noticed by the earlier investigators in the vicinity of the critical solution temperature has been discussed in detail.

REFERENCES.

Andant, A., *Thesis, Paris*, 1924.

Gans, R., *Phys. Zeits.*, 1936, **37**, 19.

Goldet, A., *Com. Rend.*, 1936, **203**, 216.

Katalinic, M., and Vrkljan, *Phys. Zeits.*, 1936, **37**, 482.

Kimura, O., *Bull. Chem. Soc. Japan.*, 1936, **2**, 57.

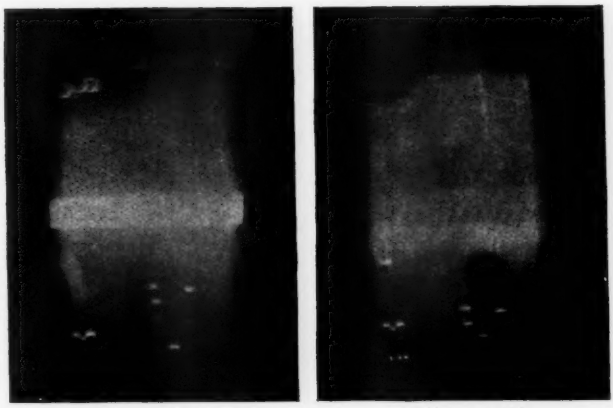


FIG. 2 (*a*). FIG 2 (*b*).

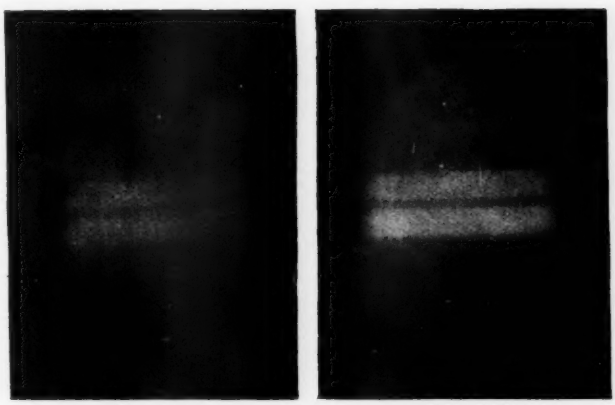


FIG. 3 (*a*). FIG. 3 (*b*).

Krishnan, R. S., *Proc. Ind. Acad. Sci.*, (A), 1934–35, **1**, 211, 915 ; 1935, **2**, 221.

————, *ibid.*, 1937, **5**, 94, 305, 407.

Ornstein, L. S., and Zernike, F., *Proc. Amsterdam*, 1914, **17**, 793 ; 1916, **18**, 1520.

————, *Phys. Zeits.*, 1918, **19**, 134 ; 1926, **27**, 761.

Placzek, C., *Phys. Zeits.*, 1930, **31**, 1052.

Rocard, Y., *Journ. de Phys.*, 1933, **4**, 165.

Rousset, A., *Com. Rend.*, 1934, **198**, 2152 ; 1934, **199**, 716.

————, *Thesis, Paris*, 1935 ; *Journ. de Phys.*, 1936, 7, 84.

Subbaramaiah, K., *Proc. Ind. Acad. Sci.*, (A), 1937, **5**, 128.

Zernike, F., *Thesis, Amsterdam*, 1915.

Zofia Szafranska, *Bull. Inter. Acad. Poloniaca, Class. Sci. Math. Nat.*, 1935, (A), **19**, 110.

THE FLUORESCENCE OF ACETONE VAPOUR.

By R. Padmanabhan.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received June 23, 1937.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

The fluorescence of acetone was first observed by Gelbke[1] the observations being extended by Damon and Daniels[2] as well as by Norrish and his co-workers. According to the latter, who have investigated the subject in detail, the fluorescence consists of three bands devoid of structure with maxima at λ 5117, λ 5572 and λ 6095. In the course of an investigation on the Raman effect in ketones, the author had occasion to take a picture of the fluorescence spectrum of acetone in the vapour state when it was observed that the bands were not devoid of structure but actually consisted of a number of diffuse bands superposed upon a continuous spectrum, the structure being most pronounced in the band with maximum at $\lambda = 5117$. Although precise measurement was not possible, the following approximate values were determined with the help of a high dispersion spectrograph.

λ 5058 (*d*), 5070 (*d*), 5081 (*d*), 5140 (*d*), 5152 (*d*), 5171 (*d*), 5186 (*s*), 5548 (*d*), 5570 (*d*) and 5594 (*d*).

The bands at λ 5140 and λ 5548 are considered doubtful.

A similar fine structure was also observed in the case of the next higher homologue, methyl ethyl ketone. These observations are evidently connected with the discrete character of the absorption spectrum of acetone vapour first observed by Norrish, Crone and Saltmarsh[3] but in view of the fact that the data given by the different workers[4,5] are conflicting, a detailed discussion is not attempted.

---

[1] Gelbke, *Jahrbuch der Radioactivitat*, 1913, **1**, 10.

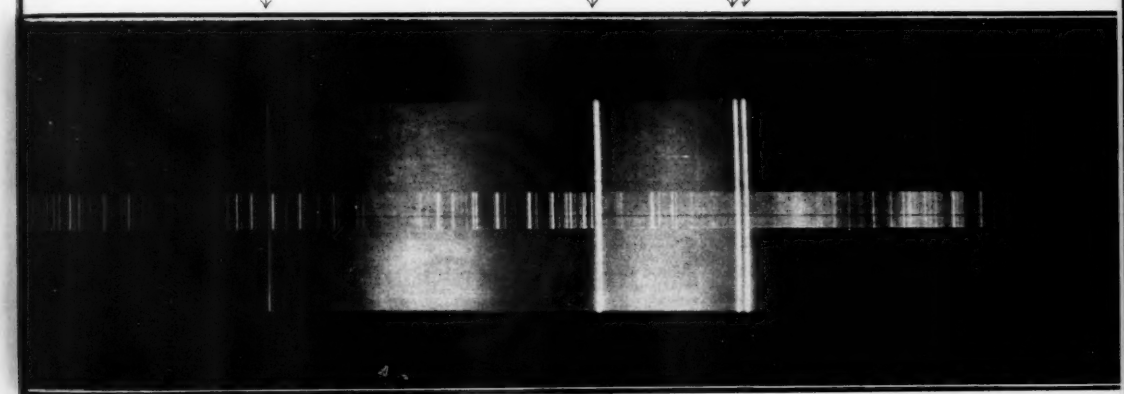
[2] Damon and Daniels, *J.A.C.S.*, 1933, **55**, 2363.

[3] Crone and Norrish, *Nature*, 1933, **132**, 241 ; Norrish, *ibid.*, 1934, **133**, 837 ; Norrish, Crone and Saltmarsh, *J.C.S.*, 1934, 1456.

[4] Bowen and Thompson, *Nature*, 1934, **133**, 571.

[5] Snow and Eastwood, *ibid.*, 1934, **133**, 908.

786-37—Printed at The Bangalore Press, Mysore Road, Bangalore City, by G. Srinivasa Rao, Superintendent, and Published by The Indian Academy of Sciences, Bangalore.



Fluorescence of Acetone Vapour.

Errata.

Vol. V, No. 5, page 497, Table VI, Column 1—

For M/20 *read* 0·0352 M
For M/40 *read* 0·0176 M

INDEX TO Vol. V (A).

AUTHORS' INDEX.

Ahmad, S. Zafaruddin, and Desai, R. D. — Heterocylic compounds—Part I. Coumarins from cyclopentanone-2-carboxylate and 4-methylcyclopentanone-2-carboxylate, 277. Part II. The synthesis of cyclopenteno-(1':2':4:3)-carbostyril derivatives, 543.

Anantanarayanan, N. .. — *See* Rau and Anantanarayanan.

Ananthakrishnan, R. .. — The Raman spectra of crystal powders.
I. The halides and sulphate of ammonium, 76; II. The chlorides and sulphates of hydroxylamine and hydrazine, 87; III. Exchange reactions: NH_4Cl and D_2O, 175; IV. Some organic and inorganic compounds, 200; V. Inorganic nitrates: water of crystallisation, 447.
The Raman spectra of some simple molecules. (Dimethyl ether, phosgene, *n*-butane, ethylene diamine, ethylene glycol, ethylene dichloride, ethylene dibromide, acetylene tetrachloride, acetylene tetrabromide and hexachloroethane), 285.

Asundi, R. K., and Samuel, R. — Some remarks on the Birge-Sponer method of vibrational extrapolation, 235.
Note on the structure of N_2^+ and its bearing on the theory of valency, 244.

Auluck, F. C. .. — A generalization of the Simson Line, 517.

Auluck, F. C., and Chowla, S. — A property of numbers, 510.

Bhagavantam, S., and Rao, A. Veerabhadra — Raman spectrum of benzene vapour, 18.

Chatterji, N. .. — *See* Singh and others.

Chowla, I. .. — On Waring's problem for cubes, 1.
On the number of solutions of some congruences in two variables, 40.
On $\Gamma(k)$ in Waring's problem and an analogous function, 269.

Chowla, S. .. — A theorem of Erdös, 37.
See Auluck and Chowla.
On some infinite series involving arithmetical functions I, II, 511, 514.

Dakshinamurti, C. .. — Light-scattering, Raman spectra and allied physical properties of some essential and vegetable oils, 385.

Desai, R. D. .. — *See* Ahmad and Desai.

Dey, B. B., and Srinivasan, T. K.		The preparation of ortho-phthalaldehydic acid, 329.
Gavanker, K. D.	..	*See* Hirwe and Gavanker.
Gogte, G. R.	..	Chemistry of β-aryl glutaconic acids. Part III. Condensations with phenolic ethers (*continued*), 535.
Gulatee, B. L.	..	Gravity, geoid and plumb-line deflections in mountainous areas, 257.
Gupta, Hansraj	..	On a conjecture of Chowla, 381.
Haq, Mohd. Israrul, and Samuel, R.		Note on the absorption spectrum of phosphorous pentaselenide vapour, 423.
Heeramaneck, V. R., and Shah, R. C.	..	Tautomerism of 2-phenyl-3-carbethoxy-4-hydroxyquinoline, 442.
Hirwe, N. W., and Gavanker, K. D.		Derivatives of salicylic acid. Part XII. Nitro-salicylic acids and their methyl ethers, 377.
Hirwe, N. W., and Patil, B. V.		Derivatives of salicylic acid. Part XI. Bromo-salicylic acids and their methyl ethers, 321.
Iyengar, K. Y. Srinivasa		*See* Swamy and Iyengar.
Iyer, P. V. Krishna	..	The distribution of the mean of Fisher's t^2 for samples from a normal population, 528.
Jayaraman, N.	..	The mineralogy and chemical composition of garnets from the schist-complex of Nellore, 148.
Jogarao, Ch. V.	..	An optical method of determining the relative coagulating powers of electrolytes, 193.
Kasbekar, G. S., and Normand, A. R.		Reaction between nitric acid and tin in presence of catalysts, I, 115.
Katti, M. C. Tummin	..	*See* Wali and Katti.
Krishnan, R. S.	..	Dispersion of depolarisation of light-scattering in colloids. I. Gold sols, 94; II. Silver sols, 305; III. Platinum, copper, selenium and tellurium sols, 407; IV. Iodine, graphite, stearic acid, vanadium pentoxide, arsenic trisulphide and ferric hydroxide sols, 499; V. Colloidal dye-stuffs, 551. Critical opalascence of liquid mixtures, 577.
Malurkar, S. L., and Srivastava, M. P.		On the differential equation of the instability of a thin layer of fluid heated from below, 34.
Narayan, K.	..	*See* Singh and others.
Narlikar, V. V.	..	A note on the mixed Tensor $T\mu^{\nu}$, 32.
Neelakantam, K., and Seshadri, T. R.		Pigments of cotton flowers. Part IV. Constitution of herbacitrin and herbacetin—new glucoside and aglucone (flavonol), 357.
Nilakantan, P.	..	X-ray studies of wood, lignin and wood-cellulose, 166.
Normand, A. R.	..	*See* Kasbekar and Normand.

Oke, B. Y. .. Lattice-theory of alkaline earth carbonates, 326.

Padmanabhan, R. .. The fluorescence of acetone vapour, 594.

Pandya, K. C., and Vahidy, T. A. The condensation of aldehydes with malonic acid in the presence of organic bases, Part VIII. The condensations of *o*- and *m*-methoxybenzaldehydes, 437.

Patil, B. V. .. *See* Hirwe and Patil.

Prasad, S. .. *See* Singh and others.

Rajam, C. V. .. Microphone actuated thyratron relay, 301.

Raman, P. K. .. *See* Ramdas and others.

Ramdas, L. A., Sreenivasiah, B. N., and Raman, P. K. Variation in the nocturnal radiation from the sky with zenith distance and with time during the night, 45.

Rangaswami, S., and Seshadri, T. R. Geometrical inversion in the acids derived from the coumarins. Part IV. The behaviour of the ethers of the *cis* and *trans* acids, 249.

Rao, A. Balankeswara .. Maxwell effect in some organic liquids, 124.

Rao, A. Veerabhadra .. *See* Bhagavantam and Rao.

Rao, B. Nagesha .. *See* Subbaraya and others.

Rao, B. S. Madhava .. On the fine structure of the Balmer lines, 56.

Rao, N. A. Narayana .. *See* Subbaraya and others.

Rao, S. Ramachandra, and Sriraman, S. The paramagnetic susceptibility of lithium, 343.

Rau, M. A. Govinda, and Anantanarayanan, N. The dipole moment and structure of some cyclic anhydrides: phthalic, succinic and citraconic anhydrides, 185.

Samuel, R. .. *See* Asundi and Samuel.
See Haq and Samuel.

Samuel, R., and Usman, M. Absorption spectra of solutions of some halides and oxyhalides of S, Se and Te, 425.

Savur, S. R. .. A new solution of a problem in inverse probability, 222.
The use of the median in tests of significance, 564.

Seetharaman, V. .. Differential invariants for path spaces of order 2, 161.
Differential invariants for path spaces of order 3, 336.

Seshadri, T. R. .. *See* Rangaswami and Seshadri.
See Neelakantam and Seshadri.

Seshadri, T. R., and Venkatarao, C. A new separation of the components of *Psoralea corylifolia*, Linn., 351.

Seth, B. R. .. On the flexure of a hollow shaft—II, 23.
On the sufficiency of the consistency-equations, 518.

Shah, R. C. .. *See* Heeramaneck and Shah.

Singh, B. K., Narayan, K., Sinha, P., Prasad, S., and Chatterji, N.	The physical identity of enantiomers. Part III. Viscosities, densities and refractivities of *d-*, *l-*, and *dl-* forms of isonitrosocamphor (stable and unstable), camphor, camphoric acid, camphoric anhydride, camphorquinone and sodium camphorate, 484.
Singh, B. K., and Sud, M. R.	Studies in the substituted quaternary azonium compounds. Part V. The molecular state of phenyldimethylazonium, phenylmethylethylazonium, phenyldiethylazonium, phenylmethylbenzylazonium, phenylpropylbenzylazonium iodides in dilute solution, 522.
Sinha, P. ..	*See* Singh and others.
Sreenivasiah, B. N. ..	*See* Ramdas and others.
Srinivasan, P. S. ..	The elastic properties of mother-of-pearl, 463.
Srinivasan, T. K. ..	*See* Dey and Srinivasan.
Sriraman, S. ..	*See* Rao and Sriraman.
Srivastava, M. P. ..	*See* Malurkar and Srivastava.
Subbaramiah, K. ..	Studies in colloid optics. I. Scattering of light by protein solutions, 128; II. Scattering of light by silicic acid sols and gels, 138.
Subbaraya, T. S., Rao, B. Nagesha, and Rao, N. A. Narayana	On the band spectrum of mercurous iodide, 365.
Subbaraya, T. S., Rao, N. A. Narayana, and Rao, B. Nagesha	On the band spectrum of cadmium iodide, 372.
Sud, M. R. ..	*See* Singh and Sud.
Swamy, S. Rama, Iyengar, K. Y. Srinivasa	X-ray analysis of the structure of a fibrous modification of tourmaline, 419.
Usman, M. ..	*See* Samuel and Usman.
Vahidy, T. A. ..	*See* Pandya and Vahidy.
Vaidyanathaswamy, R. ..	A remarkable property of the integers Mod N, and its bearing on group-theory, 63.
Venkataramiah, H. S. ..	The magnetic susceptibility of copper amalgam, 532.
Venkatarao, C. ..	*See* Seshadri and Venkatarao.
Venkatarayudu, T. ..	On the linear algebra of classes of elements in a finite Abelian group, 433.
Wali, M. A., and Katti, M. C. Tummin	Chemical examination of the constituents of *Hydrocotyle asiatica*, I, 109.

TITLE INDEX.

Abelian group, finite, linear algebra of classes of elements (Venkatarayudu), 433.

Absorption spectra of solutions of some halides and oxyhalides of S, Se and Te (Samuel and Usman), 425.

Absorption spectrum of phosphorous pentaselenide vapour (Haq and Samuel), 423.

Aldehydes, condensation, with malonic acid in the presence of organic bases, Part VIII (Pandya and Vahidy), 437.

Azonium compounds, substituted quaternary, studies, V (Singh and Sud), 522.

Balmer lines, fine structure (Rao), 56.

Band spectrum of cadmium iodide (Subbaraya and others), 372.

Band spectrum of mercurous iodide (Subbaraya and others), 365.

Coagulating powers of electrolytes, relative, optical method of determining (Jogarao), 193.

Colloid optics, studies, I, II (Subbaramaiah), 128, 138.

Congruences in two variables, some, number of solutions (Chowla), 40.

Conjecture of Chowla (Gupta), 381.

Consistency-equations, on the sufficiency (Seth), 518.

Cotton flowers, pigments, IV (Neelakantam and Seshadri), 357.

Critical opalescence of liquid mixtures (Krishnan), 577.

Differential equation of the instability of a thin layer of fluid heated from below (Malurkar and Srivastava), 34.

Differential invariants for path spaces of order 2 (Seetharaman), 161.

Differential invariants for path spaces of order 3 (Seetharaman), 336.

Dipole moment and structure of some cyclic anhydrides: phthalic, succinic and citraconic anhydrides (Rau and Anantanarayanan), 185.

Enantiomers, physical identity, III (Singh and others), 484.

Erdös, a theorem (Chowla), 37.

Fisher's t^2, distribution of the mean, for samples from a normal population (Iyer), 528.

Flexure of a hollow shaft—II (Seth), 23.

Fluorescence of acetone vapour (Padmanabhan), 594.

Garnets from the schist-complex of Nellore, mineralogy and chemical composition (Jayaraman), 148.

Geometrical inversion in the acids derived from the coumarins, IV (Rangaswami and Seshadri), 249.

Glutaconic acids, β-aryl, chemistry, III (Gogte), 535.

Gravity, geoid and plumb-line deflections in mountainous areas (Gulatee), 257.

Heterocyclic compounds—I, II (Ahmad and Desai), 277, 543.

Hydrocotyle asiatica, chemical examination of the constituents, I (Wali and Katti), 109.

Integers Mood N, remarkable property, and its bearing on group-theory (Vaidyanathaswamy), 63.

Inverse probability, a new solution of a problem in (Savur), 222.

Lattice-theory of alkaline earth carbonates (Oke), 326.

Light-scattering in colloids, dispersion of depolarisation, I, II, III, IV, V (Krishnan), 94, 305, 407, 499, 551.

Light-scattering, Raman spectra and allied physical properties of some essential and vegetable oils (Dakshinamurti), 385.

Magnetic susceptibility of copper amalgam (Venkataramiah), 532.

Maxwell effect in some organic liquids (Rao), 124.

Median, the use, in tests of significance (Savur), 564.

Mother-of-pearl, elastic properties (Srinivasan), 463.

Nitric acid and tin, reaction between, in presence of catalysts (Kasbekar and Normand), 115.

Numbers, a property (Auluck and Chowla), 510.

Ortho-phthaladehydic acid, preparation (Dey and Srinivasan), 329.

Paramagnetic susceptibility of lithium (Rao and Sriraman), 343.

Psoralea corylifolia, Linn., a new separation of the components (Seshadri and Venkartarao), 351.

Radiation from the sky, nocturnal, variation in the, with zenith distance and with time during the night (Ramdas and others), 45.

Raman spectra, light-scattering and allied physical properties of some essential and vegetable oils (Dakshinamurti), 385.

Raman Spectra of crystal powders, I, II, III, IV, V (Ananthakrishnan), 76, 87, 175, 200, 447.

Raman spectra of some simple molecules (Dimethyl ether, phosgene, *n*-butane, ethylene diamine, ethylene glycol, ethylene dichloride, ethylene dibromide, acetylene tetrachloride, acetylene tetrabromide and hexachloroethane) (Ananthakrishnan), 285.

Raman spectrum of benzene vapour (Bhagavantham and Rao), 18.

Salicylic acid, derivatives, XI (Hirwe and Patil), 321.

Salicylic acid, derivatives, XII (Hirwe and Gavanker), 377.

Series, infinite, involving arithmetical functions, I, II (Chowla), 511, 514.

Simson Line, generalisation (Auluck), 517.

Structure of N_2^+ and its bearing on the theory of valency, note (Asundi and Samuel), 244.

Tautomerism of 2-phenyl-3-carbethoxy-4-hydroxy-quinoline (Heeramaneck and Shah), 442.

Thyratron relay, microphone actuated (Rajam), 301.

$T_\mu{}^\nu$, mixed tensor, a note (Narlikar), 32.

Tourmaline, X-ray analysis of the structure of a fibrous modification (Swamy and Iyengar), 419.

Vibrational extrapolation, some remarks on the Birge-Sponer method (Asundi and Samuel), 235.

Waring's problem for cubes (Chowla), 1.
Waring's problem, on $\Gamma(k)$ in, and an analogous function (Chowla), 269.
Wood, lignin and wood-cellulose, X-ray studies (Nilakantan), 166.
X-ray analysis of the structure of a fibrous modification of tourmaline (Swamy and Iyengar), 419.
X-ray studies of wood, lignin and wood-cellulose (Nilakantan), 166.

NOTICE TO AUTHORS

Scientific papers intended for publication in the *Proceedings of the Indian Academy of Sciences* can be accepted only when they are communicated by a Fellow of the Academy whose duty shall be to satisfy himself that such communications are fit to be read at the Meeting of the Academy and published in its *Proceedings*.

Papers should not ordinarily exceed fifty pages of foolscap. MSS. should be either typewritten or written in legible hand on one side of the paper. All papers should be carefully revised by the authors and should be absolutely in final form for printing. Position for text-figures should be indicated. Each paper shall conclude with a critical summary not exceeding 350 words.

Drawings, diagrams or other illustrations should be made on larger scale (preferably twice the size) than the ones in which they are intended to appear. They should be done in Indian ink on bristol board with lettering in pencil. Scale of magnification of camera lucida tracings should be indicated by the side of drawings. In certain special cases arrangements will also be made for monochrome lithographic and other colour plates. Reduction of illustrations desired should be indicated in pencil. Appropriate legends should accompany all drawings. Names of authors are to be marked in pencil on the left-hand corner of drawing sheets. Photomicrographs should be securely mounted with colourless paste.

All tables, quotations and footnotes which will be set hereafter (beginning from Vol. I, No. 2) in types smaller than the text, should be typewritten on separate sheets and placed with the text in proper sequence. Footnotes should be numbered in Arabic numerals.

References to literature in the text should be given, whenever possible, in chronological order, only the names of authors and years of publication, in brackets, being given. They should be cited in full after the summary, the authors' names following in alphabetical order. Thus,

Name or Names of authors ; Name of Journal (abbreviation) with a single underline ; Year of publication ; Number of volume with a double underline ; and lastly Page. The following would be a useful illustration :—

Bergmann and Stather. . . . . Z. Physiol. Chem., 1926, 152, 189.

Two copies of slip-proof and wherever possible, a page proof for final revision will be sent to authors. All corrections are best made on the slip-proof which should be transmitted to the Office of the Academy. All proof corrections involve heavy expenses which would be negligible if the papers are carefully revised by the authors before submission.

Authors will be supplied with fifty copies of the contribution gratis and may buy additional copies at a small price if intimation is given at the time of returning the slip-proof.

CONTENTS

Dispersion of Depolarisation of Light-Scattering in Colloids. Part IV. Iodine, Graphite, Stearic Acid, Vanadium Pentoxide, Arsenic Trisulphide and Ferric Hydroxide Sols . . . R. S. KRISHNAN 499

A Property of Numbers . . . . F. C. AULUCK AND S. CHOWLA 510

On Some Infinite Series Involving Arithmetical Functions. S. CHOWLA 511

On Some Infinite Series Involving Arithmetical Functions (II) . . . . . S. CHOWLA 514

A Generalization of the Simson Line . . . FAQIR CHAND AULUCK 517

On the Sufficiency of the Consistency-Equations . . B. R. SETH 518

Studies in the Substituted Quaternary Azonium Compounds. Part V. The Molecular State of Phenyldimethylazonium, Phenylmethylethylazonium, Phenyldiethylazonium, Phenylmethylbenzylazonium, Phenylpropylbenzylazonium Iodides in Dilute Solution. . . . . BAWA KARTAR SINGH AND MELA RAM SUD 522

The Distribution of the Mean of Fisher's t^2 for Samples from a Normal Population . . . . . P. V. KRISHNA IYER 528

The Magnetic Susceptibility of Copper Amalgam . . . . . H. S. VENKATARAMIAH 532

Chemistry of β-Aryl Glutaconic Acids. Part III. Condensations with Phenolic Ethers *(Continued)* . G. R. GOGTE, M.Sc., PH.D. 535

Heterocyclic Compounds. Part II. The Synthesis of Cyclopenteno-(1' : 2' : 4 : 3)-carbostyril Derivatives . . . . . S. ZAFARUDDIN AHMAD AND R. D. DESAI 543

Dispersion of Depolarisation of Light-Scattering in Colloids. Part V. Colloidal Dye-Stuffs . . . . . R. S. KRISHNAN 551

The Use of the Median in Tests of Significance . . S. R. SAVUR 564

Critical Opalescence of Liquid Mixtures . . . R. S. KRISHNAN 577

The Fluorescence of Acetone Vapour . . . . R. PADMANABHAN 594